Sveriges lantbruksuniversitet
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A comparison of two treatment methods to reduce internal phosphorous cycling in lakes: surface versus injection application

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En jämförelse av två behandlingsmetoder för att minska den interna fosforbelastningen i sjöar

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Abstract

When external nutrients have been reduced from a lake, the internal loading can still be high due to a heavy load of phosphorous (P) in the sediments. Aluminium (Al) treatment has been used for several decades to permanently bind P in sediments to prevent further internal loading. The common method is by surface application of an Al salt. In recent years the method has been developed where a slurry of Al salt is injected directly into the sediments. In this study the efficiency and costs of injection application were compared to previous studies where surface application was used. The results presented in this study indicated that the Al:P ratio in the lakes did differ much, and would thus imply that the binding efficiency is similar for the two application methods. When treatment cost was compared to the amount of P bound by Al in the sediment, the results were also similar, suggesting both methods were equally beneficial for removing excess P from the P cycle in lakes.

Keywords: eutrophication, restoration, aluminium, phosphorous

Sammanfattning

Den interna belastningen i sjöar kan fortsätta att bidra till övergödning trots att externa källor av näringsämnen har minskats. Övergödningen orsakas av fosfor (P) i sedimenten vilket kan fortsätta att frigöras till vattenmassan. Aluminium (Al) har i flera decennier använts för att permanent binda Al i sedimenten och därmed minska den interna belastningen. I den vanligaste appliceringsmetoden tillsätts ett aluminiumsalt från sjöytan. Saltet fälls sedan ut sjösedimentet och binder till P i sedimentet för att förhindra intern belastning. Under senare år har metoden utvecklats där aluminiumsaltet injiceras direkt i sjösedimenten. Denna studie har undersökt bindningseffektiviteten och kostnaderna med injiceringsmetoden och jämfört resultatet med tidigare studier där ytfällning har använts. Resultatet visar att Al:P kvoten var lika i båda metoderna, vilket tyder på att båda metoderna är likvärdiga att avlägsna fosföröverskottet i sjöar.

Nyckelord: övergödning, restaurering, aluminium, fosfor

Popular science summary

Imagine a thick green carpet covering your favourite lake when you are ready for a swim. Not very nice is it? The release of nutrients from human activities has increased the pressure of aquatic water systems. Eutrophication of lakes and streams is caused by excessive nutrients which often increases the biomass of phytoplankton. Phosphorous (P) is the main nutrient in fresh water systems causing algae blooms. Restoration methods are thus needed to reduce P, and in some cases it is not sufficient to only reduce the external input of nutrient sources but other measures needs to be taken to deal with P stored in the lake sediments.

For decades salts containing aluminium (Al) have been used to treat lakes suffering from release of P. Al can efficiently bind to P in lake sediments, and prevent P its release from sediments to the waterbody. Low oxygen in bottom waters, wave turbulence and fishes searching for food in the sediments are a few natural ongoing processes causing P release. Since the first Al treated lakes during the late 1960s, Al salt has been applied directly to the water surface and then slowly precipitated towards the sediments where it binds to the P. Recently, a method has been developed where the Al instead is injected into the sediments. This injection method was developed minimize effects on biota in the water body and more efficiently bind P.

This study investigated two lakes south of Stockholm that were both treated by injection application of Al; Flaten and Långsjön. The results of how much P was bound to Al was then compared to other studies were lakes had been treated with surface application of Al. The results indicated that the binding efficiency was similar in both application methods. The costs for the two different methods were also compared, with a similar result.

As a conclusion, both methods reduced the amount of P in the water body and the binding efficiency was similar. In the future it would however be recommended to investigate the question further.

Table of contents

List of Tables

List of Figures

1 Introduction

When external sources of nutrients have been reduced, internal loading of phosphorous from lake sediments can still contribute to a high lake productivity. Aluminium (Al) and iron (Fe) are two metals commonly used to decrease the internal loading of phosphorous (P) in lakes. Compared to Fe, Al has the advantage of not being sensitive to changes in redox states. Al salts have been used for decades, especially in Sweden and USA to treat eutrophic lakes. Långsjön was the first lake to be treated with aluminium sulphate in 1968 to reduce the internal loading (Cooke et al. 2005). Since then more than 100 lakes have been treated with Al to reduce internal loading in lakes (Huser 2015).

Two different salts have primarily been used in treatment; aluminium sulfate, also known as alum, and poly-aluminium chloride (PAC). In USA, alum is the most frequently used salt to treat eutrophic lakes, whereas PAC is primarily used in Europe. Al salts have been used in treatment of eutrophic lakes for decades (Huser 2014). Al salts are favorable in treatment purposes since freshly formed Al hydroxide, $Al(OH)_3$ binds strongly to inorganic forms of P (Rydin and Welch 1998; Lewandowski et al. 2003; Cooke et al. 2005).

There are different techniques available to apply Al salts. In a newly developed technique Al is injected directly into the sediments. The more commonly used method is through application of a slurry in the water column where it settles to bind P in the sediment. The most common sorption sites for P in sediments are Al, Fe and calcium (Huser and Pilgrim 2014). A high content of silicon, calcium and sulphate ions and dissolved organic content in lakes has proven to be an effective environment for treatment with Al (Cooke et al. 2005).

The main objective of this study was to determine if injection of Al into the sediments would lead to a more efficient Al binding of P compared to the more commonly used method surface application of Al salts. In order to study the efficiency

of the injection method, a P fractionation was done according to Psenner et al. (1988) and modified by Hupfer et al. (2005) and the resulting data from the P fractionation were compared to results from previous studies to see if there was a difference in Al binding efficiency. Finally the economic costs from the two methods were compared to see which is more cost efficient.

1.1 Eutrophication and restoration

Phosphorous is often considered the limiting nutrient for algal growth in lakes (Schindler et al. 1974). This is commonly due to an excess of other dissolved nutrients relative to P in waterbodies. A larger supply of P from e.g. sewage sludge, or runoff from farms and households thus increases algal growth and productivity in lakes. Eventually when large algal mass dies and decomposes, oxygen is consumed as bacteria degrade the organic matter, which can cause oxygen depletion that negatively affects the fauna in the lake. The phenomena with lakes receiving large amounts of nutrients is commonly called eutrophication (Schindler et al. 1974). Cultural eutrophication is a term often used when the nutrients derived from human activities increase productivity in lakes (Baird and Cann 2008).

There are different methods used to restore lakes and other waterbodies with a high load of internal nutrients. The different methods are divided into categories depending on their main objective. These techniques can be based on removal of sediments, increasing the oxygen concentration or control excessive macrophyte biomass and problems caused by algae blooms (Cooke et al. 2005). Addition of low-nutrient water can be done to reduce the nutrient concentration for the algae. The first step to improve the condition of the lake, however, is to reduce the inflow of external nutrients from sources such as urban and agricultural areas.

Best management practices, BMPs, are the most important measure to reduce external sources of P. Procedures such as conservation tillage, terracing and contour ploughing, street sweeping, elimination of combined sewer systems etc. are done to protect surface water from non-point sources (Novotny and Olem 1994; Fox 1999; Sharpley et al. 2000). Stream P precipitation, constructed wetlands and ponds and riparian repair and buffer zones are a few structural and chemical BMPs to protect lakes and other water bodies (Cooke et al. 2005). Wetlands are a naturally occurring element in nature with the capacity to store and retain material. The unique characteristics of wetlands with permanent or seasonal saturation with, water make them biologically diverse and productive ecosystem. The perhaps most important function is their ability to filter water and they can be used to treat

agricultural and urban runoff and waste in constructed wetlands (Kadlec and Knight 1995).

The surrounding terrestrial habitats of water bodies have a major influence on the conditions of the water. The riparian zones between lakes or streams and land have a large influence on the water quality. One of the functions with riparian zones is the reduction of surface and sub-surface runoff volume. The zone minimizes the concentration of pollutants and protect the banks from erosion (Dosskey 2001). Grazing livestock, increased water velocity and volume, straightening of the river, are some factors that might harm the riparian zones (Cooke et al. 2005). The increased pressure can cause an increase in pollution of adjacent waterbodies. Buffer zones are established as a measure to reduce the pollution of agricultural land of rivers and lakes. The vegetated zone function as a physical and biochemical barrier of against pollution sources (Muscutt et al. 1993, Wall et al. 2001; Dosskey 2001; Brinson et al. 2002; Fiener and Auerswald 2003). Cattle exclusion from riparian zones is also an important step to minimize the related consequences of vegetation loss, soil compaction and collapse of the river banks (Armour et al. 1991).

Even when external P sources are controlled, historical external P load is often accumulated in lake sediments. This historical load continues to provide nutrients to the water column minimizing the effect of external nutrient reductions. In order to restore the lake, the old P stored in the sediments must be taken care of. With geoengineering, such as Al treatment, the ecological status of a lake can be improved by manipulation of biogeochemical processes (Mackay et al. 2014). In some cases, it is more cost efficient to only treat the lake instead of reduce all the external nutrient loads (Mackay et al. 2014).

There are numerous internal measures to reduce P or improve the water quality of the lake (Cooke et al. 2005). Food-web manipulation is a method where planktivorous fish are removed as a method to increase the biomass of zooplankton. The zooplankton feed on the algae, which will decrease in biomass (Shapiro et al. 1975). This method is usually short-lived, however, if the source of the problem (nutrients) is not controlled (Cooke et al. 2005). Artificial circulation is a technique often applied to improve the concentration of dissolved oxygen to prevent thermal stratification. It can also improve the binding between Fe and P, assuming adequate Fe exists in the sediment, because redox conditions improve and Fe will likely be found in the ferric, Fe^{3+} form, where it can bind P in the sediment. Hypolimnetic withdrawal is another technique where nutrient enriched hypolimnetic water is siphoned or pumped from the lake. This method has proven to be effective

to reduce the concentrations of surface P and improve the oxygen content in the deeper part of the waterbody (Cooke et al. 2005).

In eutrophic lakes an efficient method to reduce algae growth and macrophytes is to remove the upper sediments. By sediment removal shallow lakes are made deeper which restricts the internal loading and control the growth of macrophytes. With sediment removal the nutrient enriched layers are eliminated from the lake as well, which decreases the nutrient release and further reduces internal loading (USEPA 2003). Advantages with sediment dredging is its long-term effect since the source for internal loading is removed and not bound in place as with inactivation of P. The method is however rather expensive and disposal sites for the material are required (Cooke et al. 2005).

Addition of Fe is another method that has been applied to shallow polymictic lakes. Under oxic conditions, P will be adsorbed onto amorphous ferric hydroxides, $FeOOH \approx P$. In treatments with Fe, artificial aeration is often used as well in order to keep the sediments oxidized. The aeration is added to avoid anoxic conditions where the Fe will be reduced into ferro form, which is much less efficient at binding P (Hansen et al. 2003).

1.2 Aluminium salts

Aluminium is the most abundant metal found in the Earth's crust, where it constitutes around 8 % (Driscoll and Schecher 1990). It is not an essential nutrient for organisms, and does not accumulate in living tissue. In nature it is only found in association with other elements, i.e. minerals and rocks. Schale, sandstone and carbonates generally consists of the largest amount of Al in decreasing order. In the lithosphere, Al is mainly associated with high crystalline alumino-silicate minerals.

Al is highly insoluble in aqueous solutions, but at pH values below 6 and above 8 it becomes more soluble and may be mobilised to aquatic environments. Al exist in the Al^{3+} form only (Chang 2007). Al in soil water is mainly associated with organic compounds. In aqueous solutions, Al can be found in various inorganic complexes together with OH^-, F^-, SO_4^{2-}, PO_3^{3-}, H_4SiO_4, and $HCO3^-$ (Driscoll and Schecher 1990).

In surface waters, pH has a substantial impact on the Al speciation. As mentioned earlier, Al becomes soluble at low pH values. Almost exclusively, dissolved Al is present as an aquo form, Al^{3+}, at low pH values. With increasing pH, Al forms

complexes with OH^- through hydrolysis, such as $Al(OH)^{2+}$ and $Al(OH)_2^+$. Under pH values between 4.5- 6.0, the inorganic forms of Al are the most dominant, but organic forms of alumina-organic solutes are also a major component (Driscoll and Schecher 1990).

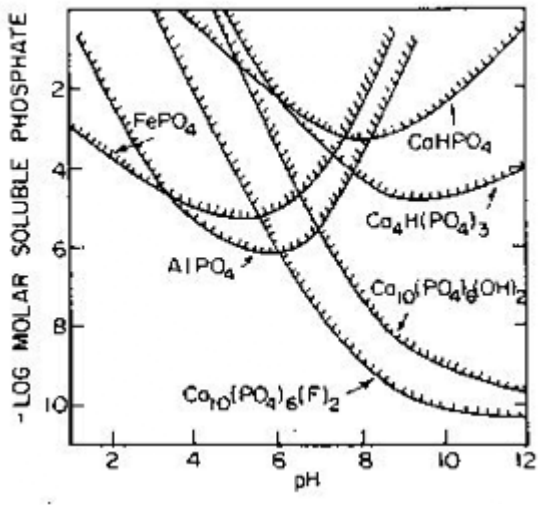

Figure 1. Predominance picture. From Morgan and Stumm 1996

There are, in general, three main bonding types between Al and P; (1) adsorption to Al hydroxide, (2) binding to the products of hydrolysis (3) metallic bonding. When P is adsorbed to Al hydroxide, phosphate and particulate matter are precipitated with the formed floc of hydroxide. The flocculent has a high P adsorption capacity (Naturvårdsverket 2009). When an Al salt, e.g. alum is dissolved in water at neutral pH the following reaction occur:

$$Al_2(SO_4)_3 \cdot 14H_2O + 6H_2O \rightarrow 2Al(OH)_3(s) + 3{SO_4}^{2+} + 6H^+ + 14H_2O \qquad \text{(Eq. 1)}$$

In this reaction Al^{3+} is bound to double OH-bridges in the newly formed hydroxide, which allows a polymerisation in the water column. When amorphous hydroxide polymerises, a flocculation and precipitation occurs in the water column. The flocculant can precipitates both dissolved P and particulate matter in the water column (Naturvårdsverket 2009). The precipitated floc will settle on the sediment surface and within time migrate into the deeper part of the waterbody (Huser et al. 2011).

The amount of P bound to the hydroxide complex varies. Efficient binding is obtained if Al salt is added where the concentration of phosphate is as high as possi-

ble. This is because as the amorphous $Al(OH)_3$ begins to crystalize after forming, and surface area and binding capacity begin to decrease (Berkowitz et al 2006, de Vincente et al. 2008). At neutral pH, a reaction between the Al salt and water molecules occurs before an Al hydroxide complex is formed:

$$Al^{3+} + H_2O \rightarrow Al(OH)^{2+} + H^+, Al(OH)^{2+} + H_2O \rightarrow Al(OH)_2{}^{+} + H^+ \quad \text{(Eq. 2)}$$

Phosphate can form complexes with the hydrolysis products' and protons are released:

$$SAl^{3+} + (3-x)H_2O + xH_2PO_4{}^{-} \rightarrow Al(OH)_{3-x}(H_2PO_4)_x + (3-x)H^+ \quad \text{(Eq. 3)}$$

If the dihydrogen phosphate precipitates with Al hydroxide, hydroxide ions are released accordingly:

$$Al(OH)_3 + xH_2PO_4{}^{-} \rightarrow Al(OH)_{3-x}(H_2PO_4)_x + xOH^{-} \quad \text{(Eq. 4)}$$

A more uncommon binding between phosphate and Al is one where the phosphate binds directly to the Al ion that occurs under high phosphate concentrations in e.g. wastewater treatment. This formation creates variscite, a hydrated Al phosphate mineral with the chemical formula $AlPO_4 \cdot 2H_20$ (Gillberg 1996).

Naturally occurring Al complexes have a low solubility in aqueous solutions and are thus generally solid in soil. When conditions become more acidic, the solubility increases and Al may be released into the water. During the transport from soil water to streams and lakes, Al is mainly bound in organic complexes in soil water. These organic complexes precipitate during transport and the Al is released as inorganic complexes (Gensemer and Playle 1999). Even under these conditions, Al can still bind P in lake sediment (Huser and Rydin 2005).

An increase in concentration of inorganic Al in freshwater systems under acidic conditions may pose a threat to fish, species within the *Salmonidae* family are particularly sensitive (Gensemer and Playle 1999). $Al(OH)_3$ precipitates on the gills of the fishes which causes a disturbance in the osmoregulation. The disturbance stimulates an overproduction of mucus, which obstructs respiration (Driscoll and Schecher 1990). Nymphs of mayflies and other benthic fauna may also suffer problems with oxygen uptake due to Al hydroxide (Smeltzer 1990).

Like Ca^{2+} and Mg^{2+} ions, Al^{3+} compete with complexing agents with oxygen-atom donor sites like phosphate groups and other organo-phosphate compounds (Krewski et al. 2007). The metal might also interfere with the metabolism of Ca^{2+} and Mg^{2+} (Driscoll and Schecher 1990). Humans might be exposed to Al through a wide range of different pathways, such as food, water or inhalation of fumes and dust. The understanding of the bioavailability and intake for humans is unfortunately poor (Driscoll and Schecher 1990).

The result of several studies investigating the effects on benthic fauna by alum are compiled in Cooke et al (2005). The overall long-term effects of alum treatment observed *in situ* are small and abundance and diversity usually increase over the long-term due to improved conditions in the treated lake (Huser and Köhler 2012). In a study by Smeltzer (1990) benthic invertebrate population was examined in Lake Morey, Vermont. The lake was treated with alum (35-45 mg L^{-1} $CaCO_3$) in 1986 to reduce the algae blooms associated by internal P loading. The following year the density of animals decreased by 90 % in the upper sediments. The dosage was measured to be 200 μg Al L^{-1} in the affected sediment layers. A few years post treatment taxa richness began to increase and two additional species colonized the lake (Smeltzer 1990).

1.3 Phosphorous exchange between sediments and lake water

Lake sediments can be a sink as well as a source of P, and are thus vital to the P cycle in lakes (Boström et al. 1988). Different morphology, water retention time, historical loading of P and properties of the drainage basin affect the P retention of lakes. The deposition of P in lakes may occur through six different mechanisms. (i) Detrital P mineral sedimentation from the watershed. The deposition occur mainly near the shore since the major part of this fraction contains material settling rapidly. (ii) P can also be adsorbed or precipitate with inorganic compounds. A subdivision can be made according to Williams and Mayer (1972) (a) coprecipitation of P and Fe and Mg, (b) adsorption to clays and amorphous oxides and (c) P associated with carbonates. (iii) P sedimentation with allochtonous and (iv) autochtonous organic matter. (v) P may also be taken up or assimilated to the water column by biota. (vi) Adsorption directly onto particles in the sediment from dissolved P in the water (Boström et al. 1988).

The most common sorption sites for P in lake sediments are provided by Fe, Al and Ca (Huser and Pilgrim 2014). When a P fractionation is done six different fractions are obtained (Psenner et al. 1988). Among the fractions P bound to Fe, Al

and Ca is obtained together with organically bound P and easy available, or loosely bound P (Rydin 2006).

1.3.1 Mobilization processes

Temperature, pH and redox potential are the main factors influencing the mobilization and fixation of P. Changes in temperature affect biological activity, where an increase in temperature increase biological activity. Increased activity of the microbial community may influence the chemical environment and thus the chemical and physical mobilization processes and transport of P. The redox potential decreases as the microbial activity increases, and may alter the electron acceptors in the mineralization of organic matter. Less reduced products might change the P cycle in lakes through H_2S, CH_4 etc (Boström et al. 1988).

High primary production can increase the pH in the lake. With an increase in lake pH two major effects occur. First the P binding capacity of Fe and Al compounds decreases due to ligand exchange reactions where orthophosphate is replaced with hydroxide ions. Second, Fe^{2+} and orthophosphate can be released from sediments under anaerobic conditions and then mix into the water column. After mixing, only some of the P will form a complex with the reprecipitated Fe^{3+} (Boström et al. 1988). Redox potential is the third factor influencing the mobilization of P in lakes. The pool of Fe^{3+} might be reduced to Fe^{2+} if the redox potential is below 200 mV. This results in a release of P associated bound to Fe^{2+} into the water body.

1.3.2 Transport processes

Dissolved P in pore water is an important fraction in the sediments because it is directly exchangeable with the water. It is also an indicator of the P saturation level in sediments. The fraction is usually the smallest ($\leq$ 1 %) of the total P. The main transport mechanism for P from sediments to hypolimnetic water is molecular diffusion. The upward diffusion of pore water is caused by a concentration gradient at the sediment-water interface (Boström et al. 1988).

In shallow lakes, turbulence caused by wind can also affect P exchange. The concentration gradient is amplified when more P is dispersed into the lake water, which results in a diffusion increase. Pore water and lake water can also be mixed mechanically by the turbulence. P might also be released from sediment particles due to waves and turbulence caused by wind (Welch and Cooke 2005).

Exchange between pore water and lake water can be affected by feeding activities of benthic fishes and macroinvertebrates as well. This phenomena is called biotur-

bation and results in an upward transport of sediment particles (Boström et al. 1988). Recent research has shown that feeding by benthic fishes can increase sediment mixing, potentially leading to more P release from the sediment (Huser et al. 2015b).

1.3.3 Internal loading in different lake types

Depending on lake morphology, mobilization and transport processes can vary. These differences affect the behaviour of internal loading. Diffusion and redox controlled mobilization of P are often the primary mechanisms in deep and stratified lakes. The transport rate is generally slow in deep lakes, but this is counteracted by a long duration of P release. Circulating water masses in shallow lakes creates a heterogeneous environment for the lake sediments. Anaerobic sites or zones are favourable for P mobilization processes. These sites are given by high pH and temperature and microstratifications formed by moving water masses. The heterogeneous environment can however cause a slower mobilization process since immobilization and retention processes occur at the same time (Boström et al. 1988).

1.4 Aluminium treatment

Aluminium has been used to reduce the internal loading of P for many decades (Landner 1970, Kennedy and Cooke 1987, Rydin and Welch 1998, Lewandowski et al. 2003, Huser et al. 2011). Some advantages with treatment using Al salts are that the Al poses no threat of toxicity with correct dosing. Al has a high adsorbing capacity of P with an almost irreversible binding. Another advantage with Al compared to other binding agents like iron is that Al is not redox sensitive (Hansen et al. 2003). In contrast to Fe bound P, Al bound P provide a long-lasting treatment since it will not be dissolved in reducing sediments (Reitzel et al. 2005).

In a study by Welch and Cooke (1999) 21 Al treated lakes were reviewed regarding their longevity of the treatment. For dimictic lakes the effect of the treatment lasted between 5 and 20 years. The longevity of treatment in shallow polymictic lakes are usually lower, between <1 and 11 years. A more recent study by Huser et al. (2015a) determined an average longevity of 15 years (5.7 for polymictic and 21 for stratified lakes). They also estimated longevities for treatments still controlling internal P release and showed some treatments may last for 100 years or more. Generally a lower Al dose is given to shallow lakes. This because the lower water volume gives a limited alkalinity to buffer acid producing Al hydrolysis reactions (Huser et al. 2015a).

In a study by Huser et al. (2015a) 114 lakes previously treated lakes were studied. The authors suggested the longevity of an Al treatment is increased the greater the water column depth relative to the lake area. Factors such as lake shape and fetch affects the stability of the water column. The hydraulic residence time, where lower values resulted in greater longevity was also an important factor (Huser et al. 2015a).

1.4.1 Aluminium sulphate vs poly-aluminium chloride

The most common Al salts used are aluminium sulphate (alum), sodium aluminate and poly-Al chloride (PAC). Alum is a common coagulant used to treat drinking water. Alum has exclusively been used in treatments done in North America. The salt is dissolved in the lake and then spread in the whole waterbody. When the salt is added the pH decreases due to the hydrolysis reactions mentioned above. The buffer capacity of the lake is decisive for the dosage and not the amount of P. Buffers are often added to limit the pH decrease during application (Naturvårdsverket 2009). A pH target of 6.0 is often chose for application because it limits toxic effects and it is also the point of maximum formation of $AlPO_4$ (Stumm and Morgan 1996).

More recently, PAC has been used in Sweden for treatments. These solutions have a low basic content and are usually named after the amount of Al oxide Al_2O_3 in the material. PAX-18 contains thus 18 % PAC which is equivalent to 9 % pure Al. A medium basic solution such as PAX XL-60 contains more silica, about 1 %, which results in a faster flocculation. The ratio between OH- and Al- ions gives the solutions different buffer capacities. Al sulphate is generally less expensive compared to PAC.

Alum can be obtained in granular form, compared to PAC which is provided in an aqueous solution but both are generally applied to lakes in the liquid form. The granular form is often considered easier to handle compared to the solution and can be an advantage for alum. Deciding which form of Al to add is mainly determined by the expected decline in pH during treatment. In treatments done in North America, alum is usually dissolved when treatment is done, which make it possible to buffer the solution (Naturvårdsverket 2009).

1.4.2 Dosage and dosing ratio

The dosing ratio is used to minimize the amount of mobile P in the sediment and to reduce internal loading (Huser and Pilgrim 2014). The Al dose is often estimat-

ed by the amount of mobile P in the sediment and the amount of Al that would be required to bind the phosphorous (Naturvårdsverket 2009).

The inactivation of P in lakes occur through both P precipitation and inactivation. With precipitation, P is removed from the water column as the $Al(OH)_3$ settles, and with inactivation release of mobile P from sediments is prevented by the settled Al-floc (Cooke et al. 2005). When addition of Al salts occurs in neutral pH water, an amorphous floc of $Al(OH)_3$ is formed with high adsorption capacity of P and coagulation properties (Hansen et al. 2003). The purpose of the addition is to lower the initial content of P in lakes and to create a lasting control of the release of P buried in the sediments. Depending on the pH, the removal of phosphate occurs by different mechanisms. Around a neutral pH, 6.0-8.0, amorphous $Al(OH)_3$ is formed (equation 1).

For water column P precipitation, the dosage is determined by stepwise additions of $Al_2(SO_4)_3$ to the samples of lake water. This procedure is done until enough P has been removed, and a dosage for the entire lake is calculated. To estimate the dosage of Al salt to inactivate P, three different procedures are available. One of the methods developed by Kennedy (1978) is the alkalinity procedure. In this method the concentration of $Al(OH)_3$ is assumed to be related to the amount of mobile P bound in the lake sediments, since Al-P is proportional to the amount of added Al. The aim of the method is to add as much Al as available alkalinity allows but is not actually based on sediment P. This method is only applied in lakes with an alkalinity above 35 mg $CaCO_3$/L. To avoid toxic forms of Al that are available at pH levels below 6.0, the safe upper limit for post treatment dissolved Al concentration was suggested to be 50 µg/L (Kennedy 1978).

Estimated rates of net internal P loading from the sediments (Nürnberg 2009) determined from mass balance equations, have also been used to determine Al doses (Kennedy and Cooke 1982). This method is an improvement compared to alkalinity based dosing, but it is based on the internal loading rate. A rate gives how much P may be released from the sediment in a year, but gives no information about how many years of P release are contained in the sediment.

In the third method the dose is estimated through a direct determination of mobile inorganic P available in the sediment. The mobile P is defined as pore water, loosely bound and reductant soluble P. Some advantages with this procedure is that the method measures the quantity of mobile P in sediments that should be transformed to Al-P Rydin and Welch (1999) in order to reduce P release from the sediment. The Rydin and Welch (1999) procedure uses a ratio of 100:1 of Al add-

ed to Al-P formed by using the amount of mobile P in 0-4 cm layer into account when estimating the dose. With this ratio the migration of P buried at deeper depths are taken into consideration as well. To execute the method an extensive P fractionation is required, which is a disadvantage. This method has since been modified to allow for variable Al dosing that can be chosen to achieve a specific internal sediment P release rate after treatment (Huser and Pilgrim 2014).

Ratios lower than 100:1 have also been suggested as adequate to reduce internal P loading. The recommended application ratio of Al:P according to de Vincete et al. (2008b) is 10:1. In the shallow and hypertrophic Lake Sønderby a molar ratio of 4:1 was however enough to reduce the sediment release of P (Reitzel et al. 2005).

1.4.3 Al:Al-P ratio

The ratio of Al: Al-P can be measured after the treatment is done, and is the theoretical ratio when all the binding sites have been filled. The structure and composition of a lake and its sediments are some factors influencing the amount of P binding to the added Al. To achieve an effective precipitation in lakes with a low amount of P, a higher amount of Al is often required. If treated more than once with multiple lower doses, the Al:P quota for the lake is usually reduced. This is because P is gradually mobilized from the sediments, allowing time for Al binding sites to become saturated before the next treatment. This prevents crystallization of the amorphous Al-floc in the absence of P, which leads to a higher binding efficiency.

The Al:P ratio in treatments with Al has varied in different studies. Rydin et al. (2000) found ratios varying between 11.3 and 13.1 (average 12.6) in six stratified and non-stratified lakes in Washington, USA. A German hard-water lake, Süsser See, was continually treated with small doses of alum (2 mg Al L^{-1}, equivalent to 100 g m^{-2}) between the years 1977 and 1992 in order to investigate the long-term effects of Al treatment. The in situ measured molar ratio of added Al to Al-P was approximately 2.1:1 (Lewandowski et al. 2003). The conducted study emphasized the large sorption capacity of the $Al(OH)_3$ layer by its ability to adsorb P from different fractions (Lewandowski et al. 2003). It also showed that adding smaller Al doses over time lead to improved binding efficiency.

A study by Huser et al. (2011) analyzed the sediment cores of one polymictic and one dimictic lake in Minnesota four years after alum treatment with ratios of 5.6 and 9.6 respectively. In another study by Huser (2012) investigated sediment cores from six urban lakes in Minneapolis all treated with alum. The molar ratio of Al: Al-P after treatment varied between 5.6–14.5. As suggested by Berkowitz et al.

(2006) and de Vincente et al. (2006) limited amount of available P or crystallization of the $Al(OH)_3$ might be some of the explanations for the various result in the Minnesota lakes. It is also important to note that the relationship between P and Al before the treatment will also influence the post treatment ratio (Huser 2012).

The binding of Al and P in lakes may vary due to different reasons; binding may be reduced due to aging of the amorphous $Al(OH)_3$. This is particularly substantial when P crystallization occurs in the absence of P (Huser 2012). The adsorption of P to Al is also affected by the surface area of $Al(OH)_3$, and will within time decrease and limit P adsorption (de Vincente 2008). Morphology, hydrology, water chemistry and applied Al doses are different for treated lakes and will thus also influence the ratio of Al:Al-P in treated lakes (Huser et al. 2015a).

1.4.4 Resuspension and translocation

The Al floc on the sediment surface is mobile and prone to resuspension (Egemose et al. 2009) and might also be translocated to deeper areas of the lake (Huser 2012). The management of trophic state condition is usually more difficult in shallow lakes than deep ones. This is because P is easily recycled from the sediments to the surface water in shallow lakes, which make the reduction in excess nutrients more difficult to control (Welch and Cooke 2005). Wind resuspension and bioturbation together with a high pH or low ratio between iron and phosphorous maintaining a high P solubility. Calm and warm weather might stimulate reducing conditions in sediments and decrepitude of macrophytes are different mechanisms in shallow lakes resulting in a high P release from sediments (Welch and Cooke 2005). Egemose et al. (2009) suggested a 2 to 4 months' time for floc stabilization to avoid resuspension of the Al floc in shallow lakes with a high primary production. The application of Al should also be done during periods with lower resuspension (Egemose et al. 2009).

Because of the high surface area and low density of the amorphous $Al(OH)_3$ floc, movement of the aluminium hydroxide may occur after the treatment (Huser et al. 2011). In a study by Huser et al. (2011) the deep dimictic lake Harriet in Minneapolis Chain of Lakes was treated with alum in the littoral zone. Within a year, post-treatment sediment chemistry data revealed the Al floc drifted to the centre of the lake. Although the $Al(OH)_3$ was applied in the littoral zone to decrease algal growth by limiting the P available in the shallow water sediments, the overall internal loading of P was reduced in the lake (Huser el al. 2011).

Benthic feeding fishes such as the common carp (*Cyprinus carpio*) have been suggested to contribute to transport of P in lakes while searching for food in lake sed-

iments (Nikolsky 1963; Meijer et al. 1990; Chumchal and Drenner 2004). Carp contribute to release of P into the water column with a physical disturbance through bioturbation and excretion (Lamarra 1975; Breukelaar et al. 1994; Moss et al. 2002; Chumchal et al. 2005; Driver et al. 2005). The effects of nutrient release caused by carp are poorly documented. In order to estimate the release due to bioturbation factors such as sediment properties, pH, oxygen content, P-binding, availability of mobile sediment P, water column mixing and carp burrowing depth need to be estimated since they have an impact. A study by Huser et al. (2015b) showed that adult carp can dig deep into lake sediments (15 cm), whereas even individuals less than 30 cm were able to dig up to 15 cm into the sediments (Nikolsky 1963). Another study by Alikunhi (1966) showed effects of sediment mixing at 12 cm depth where carp and bream (*Abramis brama*) were present. In the same study bream appeared to be a stronger sediment burrower than carp.

1.4.5 Application processes

The more common method used, were the Al salt has been added to the lake surface and allowed to precipitate, is considered a harsh method. This kind of addition of Al may have an effect on the whole water body and the biota in the lake (Värnhed 2005). The method used in the treatment of the lakes investigated in this study, Flaten and Långsjön, was patented by the consulting company Vattenresurs AB in Stockholm. A solution of poly-Al chloride was injected a specially designed vehicle. A 20 meter long crosswise hanging spreader was attached underneath the vehicle. The spreader could be regulated in depth. For the treatment, the sediments were injected by the projecting metering tube. Programmable dosing pumps and GPS were used to inject the proper dose of Al in to the sediments and adjust for dose spatially. A precipitant was added during high pressure allowing it to be mixed into the sediments (Värnhed 2005).

1.5 My study

For my study, sediment samples from lakes Långsjön and Flaten in Stockholm were collected. The main objective of the study was to test the somewhat newer, injection method of adding Al to sediment and compare this method to the more common, surface treatment and precipitation method. The surface method has been used for several decades (Landner 1970, Kennedy and Cooke 1987, Rydin and Welch 1998, Lewandowski et al. 2003, Huser et al. 2011) and the salt is generally applied onto, or just under the lake surface. The newer, injection method was developed to apply and mix the Al directly in the sediment and minimize water column effects. The hypothesis for the study is that a direct injection will re-

duce the Al:Al-P ratio in sediment after treatment because the Al more easily comes in to contact with P before crystallization. P fractionation was done in order to distinguish between the different sorption sites for P available in the sediments and the amount of P bound to them. The binding efficiency data from my study was then compared with data from previous studies where surface applications of Al occurred. The costs for the different methods were also compared to determine which method is more cost effective.

2 Materials and methods

2.1 Study sites

The sites chosen for this study, lakes Flaten and Långsjön, situated south of Stockholm.

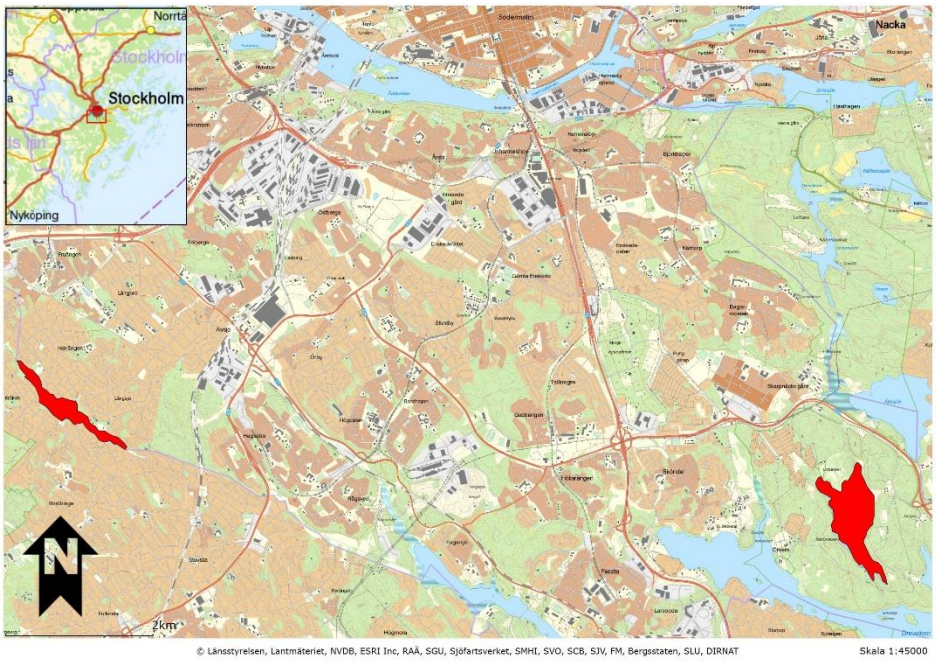

Figure 2. General map of the study sites; both lakes marked in red. Långsjön to the left, and Flaten to the right. From VISS (Vatteninformationssystem i Sverige) 2015.

Table 1. *Background information for Flaten and Långsjön*

	Flaten	Långsjön
Surface area (ha)	63	29
Mean depth (m)	7.4	2.2
Maximum depth (m)	13.6	3.3
Watershed area (ha)	403	243
Residence time (yr)	4	0.4
Al treatment (g Al m^{-2})	61 (in 2000)	75 (in 2006)
Treatment date (yr)	2000	1968, 1970, 2006

2.1.1 Flaten

Flaten is a 63 ha dimictic lake situated 10 km south from Stockholm city centre, 59° 25'01'' N, 18° 15'38'' W (Table 1). The lake is part of a larger lake system, consisting of more than 30 lakes. The catchment area is 403 ha. 70 % of the catchment area consists of hilly forest, and the area has a long tradition of being a recreational area for leisure. Residential areas reside in the northern part of the catchment. Common fish species found in Flaten are European perch (*Perca fluviatilis*), Common bleak (*Alburnus alburnus*), Silver bream (*Abramis bjoerkna*), Common bream (*Abramis brama*), Eurasian ruffe (*Gymnocephalus cernus*), Northern pike (*Esox lucius*), Common roach (*Rutilus rutilus*), Common rudd (*Scardinius erythrophtalmus*) and Tench (*Tinca tinca*) (Fränstam 2011).

75 kg of phosphorous enters Flaten annually from external sources, mainly through surface run-off from residential areas (Stockholm Stad 2000a). The lake is deep and stratified, and anoxic conditions occur annually during late summer. Some years anoxic conditions may occur during the winter and spring months.

In 2000 Flaten was treated with poly-Al chloride in an attempt to bind mobile P in the sediment. Vattenresurs AB performed the treatment during September and October 2000, when the chemical Kemwater PAX was injected into the lake sediment. Kemwater PAX is a solution of poly-Al chloride and is similar to precipitation chemicals used in wastewater treatment plants. The Al addition was done in batches, and the pH checked regularly to avoid a drop in pH (Värnhed 2005). Due to the high alkalinity in Flaten, the reported pH drop was not higher than 0.4 units, from pH 7.1 to 6.7.

Al was added to the lake sediment based on the approximate mobile sediment P content 3.3 g P m^{-2} (Rydin 1999). For lake sediments located deeper than six meters, an addition of 36 g Al m^{-2} was recommended by Rydin (1999). Because bind-

ing between Al and P in sediment is not 1:1, a ratio of 10:1 was used, for the treatment of Flaten. 40 g Al m^{-2} was added for water column depths between 6 to 9 meters. 54 g Al m^{-2} for floors between 9 and 10 meters and for areas deeper than 10 meters 70 g of Al m^{-2} was added (Värnhed 2005). The average addition of Al was 61 g m^{-2} for the entire treated area. The total treated area was equivalent to 40 ha, about 65 % of the surface area and 35 % of the lake volume. In total 270 tons of Kemwater Pax was added containing 9 % Al (Värnhed 2005).

After the treatment in 2001, the measured release of P from the sediment was less than 1 kg yearly. During the two summers after the treatment, the internal load was estimated to be 0.7 kg, whereas the internal load was 240 kg pre-treatment (Värnhed 2005). The decline in internal loading caused a decrease in the total P amount in the entire lake. After the treatment in 2000 the total P amount in the lake was 60-65 kg, which can be compared to a peak in total P mass in October 1998 with 400 kg (Värnhed 2005). The reported annual mean of the total P concentration in the epilimnion before treatment was 40-50 μg L^{-1}, whereas it was less than 10 μg L^{-1} after treatment (Stockholms Stad 2015a).

2.1.2 Långsjön

Långsjön is a 29 ha polymictic lake located in an old residential area on the border of Stockholm and Huddinge municipality, 59° 26'77'' N, 17° 96' 67'' W (Table 1). The catchment area of Långsjön is 243 ha and consists of mainly residential areas. Fish species present are representable for eutrophic lakes; European perch (*Perca fluviatilis*), Common roach (*Rutilus rutilus*), Crucian carp (*Carassius carassius*), Tench (*Tinca tinca*) and Common carp (*Cyprinus carpio*) (Fränstam 2011).

During the 1920s and 30s the lake received substantial quantities of wastewater and it was reported that only a third of the lake surface was free from vegetation during the 1940s. Långsjön became one of the first lakes in Stockholm to be treated with Al as a restoration method (Stockholm Stad 2000b).

The external loading of P to the lake is 70 kg annually, mainly coming from surface run-off from urban areas (Stockholm Stad 2000b). Shallowness combined with a low water inflow rate and long retention create a stratification layer during winter. The oxygen conditions are strained, but nowadays the presence of hydrogen sulphide is rare (Värnhed 2009). During the summer months the high amounts of P resulted in blooms of cyanobacteria, which on many occasions were toxic (Värnhed 2009).

Since early 2002, drinking water (30 L $^{-}$s) is added to decrease the water retention time and dilute P concentrations. This measure has led to a retention time of four to five months, instead of nine to ten, which is the theoretical retention time without dilution water being added (Värnhed 2009).

In a previous study by Rydin (2006), enhanced concentrations of Al bound P (Al-P) were found at sediment depths of 20 to 25 cm. These concentrations probably represent treatments done in 1968 and 1970 with alum. In 1968, 8 g of Al m^{-3} water was added which corresponds to 24 g Al m^{-2} using a mean of 3 meters for water column depth of the treated area. The treatments during 1968 and 1970 were probably not adequate to inactivate the total pool of mobile P (see section 2.3) in the sediments and, continuously high external loading of nutrients likely increased P in the sediment after treatment.

Rydin (2006) estimated that sediments deeper than 2.5 meters water column depth contained 9.3 g P m^{-2} that, over time could be released to the waterbody. In 2006, 75 g of Al m^{-2} in the form of aluminum chloride was injected into the sediments, following the same procedure as the treatment of Flaten 2000. Three years after the treatment, the P concentration in the waterbody had decreased from 140 to 35 µg L^{-1} (Värnhed 2009).

2.2 Sampling of sediment core

Three sediment cores from each lake were taken in the beginning of February 2015 with a Willner gravity sediment-coring device (Table 2). The sediments were sliced on site at intervals of 1 cm between 1 and 20 cm, and at 2 cm intervals from 20 to 40 cm. For Flaten, the samples were taken at 12.9, 11.6 and 8.3 meters water column depth. In Långsjön the samples were taken at 2.0, 2.6 and 3.0 meters depth. The samples were stored in opaque containers at 4°C before analysis.

Table 2. *Depth, temperature and concentration of dissolved oxygen at the sampling points.*

Sampling point	Depth (m)	DO (mg L^{-1})	Temperature (°C)
Flaten 1	12.9	7.1	4.0 (at 10 m)
Flaten 2	11.6	7.7	3.6 (at 9 m)
Flaten 3	8.4	9.1	3.4 (at 7 m)
Långsjön 1	2.0	4.3	2.8 (at 1 m)
Långsjön 2	2.7	2.4	4.1 (at 2 m)
Långsjön 3	3.0	2.3	3.6 (at 2 m)

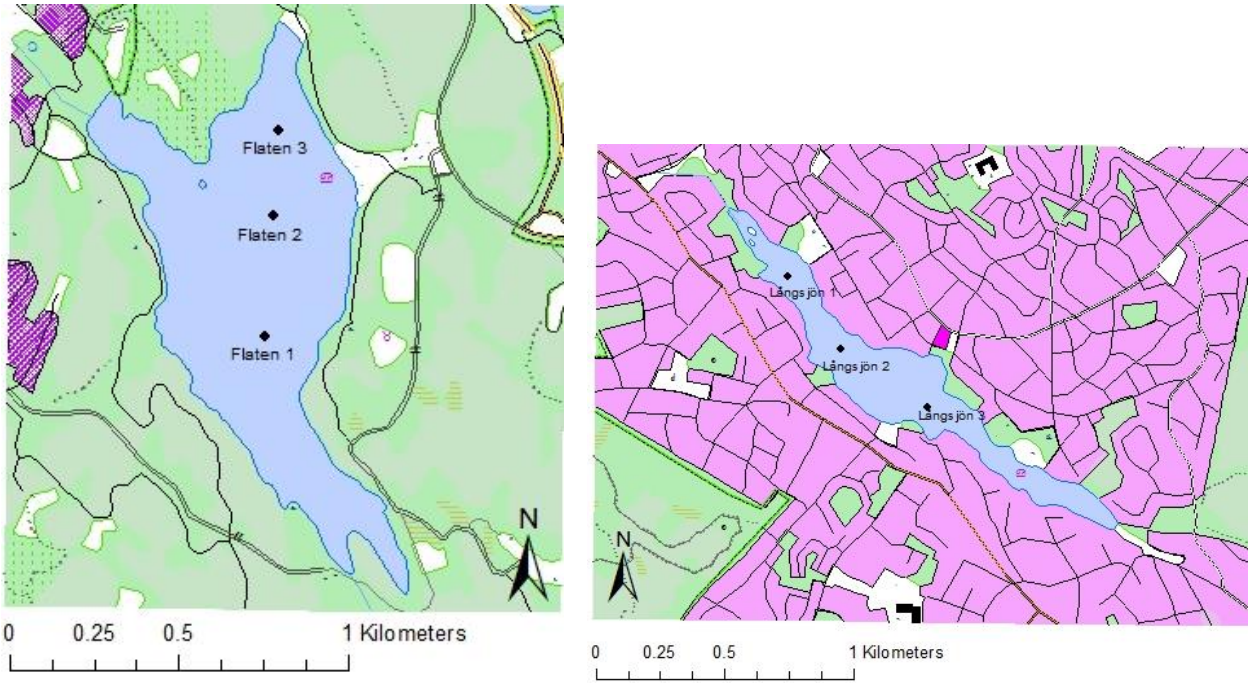

Figure 3. Sampling points in Flaten and Långsjön. From ArcGIS

2.3 Phosphorous fractionation

P fractionation was done according to Psenner et al. (1988) modified by Hupfer et al (2005). 100 to 200 mg of wet sediment was added to 15 mL centrifuge tubes. In the first fractionation step, 10 ml of double de-ionized water (MQ) was added to the tubes to extract the easy available P during two hours. In the second step 10 ml of sodium dithionite (BD) was added for one hour to reduce Fe and release P from the sediment. Next, 10 ml 0.1 M NaOH was added to extract Al bound P (Al-P, i.e. ligand exchangeable P) for 16.5 hours (NaOHrp). A portion of the NaOH extract was digested with an oxidizing agent ($K_2S_2O_8$), at 120° C in an autoclave to determine total amount of P in the extract. The difference between total P and Al-P is the amount of organic P in the sediment sample (NaOHnrp). In the final step, 10 ml of 0.5 M HCl was added to extract the P bound to calcium. Mobile P is given by the easy available P (MQ) and Fe-bound P (BD). All the fractions were later analysed in a spectrophotometer at 880 nm using the ammonium molybdate blue method (Murphy and Riley 1962).

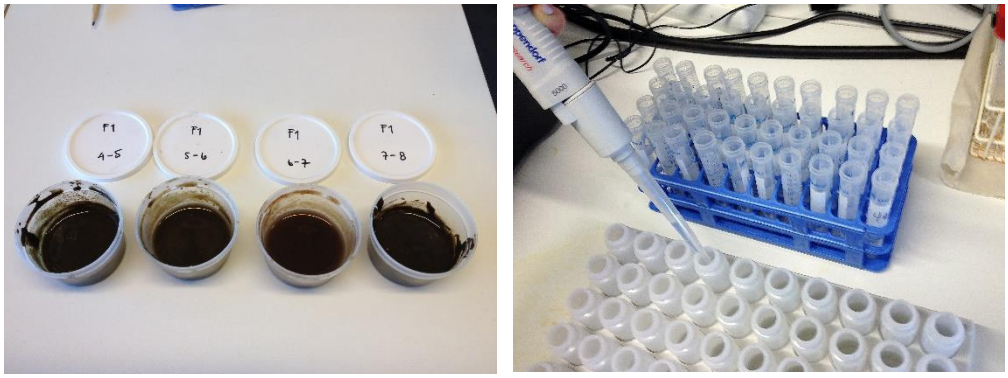

Figure 4. Pictures from the P fractionation procedure

2.4 Dry weight and loss on ignition

Water content of the samples was determined with approximately 8 g of wet sediment added to plastic containers and frozen at -70° C for approximately 24 hours. The samples were then placed in a freeze drier for 4 days. After drying in an oven at 50° C oven for 24 hours, the samples were weighed and water content was determined. The amount of dry sediment (DW) was then calculated as a percent of the total weight that remained after drying (e.g. 95 % water content and 5 % dry sediment (DW)).

To determine the organic content and estimate sediment density between 200 to 400 mg of dry sediment was placed in an oven for 550° C for two hours to determine the loss on ignition (LOI), which is used to calculate organic content and estimate sediment density (Håkanson and Jansson 1983).

2.5 Aluminium digestion

The amount of Al in the sediments was determined through an acid digestion. Between 15 to 20 mg of dried sediments were weighed and added to digestion tubes. 10 ml of 7 M HNO_3 was added and the tubes placed in an autoclave at 120° C for 30 minutes. The solution was transferred into centrifuge tubes and placed in a centrifuge for 10 minutes at 3000 rpm. 1 ml of the solution was then placed in new centrifuge tubes together with 9 ml of double de-ionized water. The samples were then analysed in an ICP-AES at 396 nm.

3 Results

3.1 Organic matter and sediment density

3.1.1 Flaten

Sediment density and organic matter content varied in the three cores from each lake (Figure 5). The sediment density was slightly lower compared to the layers above and below between 5 and 7 cm sediment depth for cores Flaten 1 and between 4 and 6 cm for core Flaten 2. The sediment density in these layers was 1.02 g cm^{-3} and the layers below 1.08 g cm^{-3}. During the experiment these layers were perceived as less compact than the other layers, which would suggest they were part of the Al treated layers. The dry matter content for core Flaten 1 and 2 varied between 4 and 20 %. The organic matter content was calculated from the loss on ignition, and varied between 15 % in the deeper layers to 40 % at the peak of 6.5 cm depth in core Flaten 1. The organic matter content was highest at 4.5 cm in core Flaten 2 with 36 % and decreased with depth.

The shallow core from Flaten 3, at 8 m, had a more consistent pattern for organic matter content, with no distinct peak as was found in cores Flaten 1 and 2. The organic matter content varied between 10 and 15 % throughout the entire core. The overall sediment density was higher in core 3 from Flaten compared to the other two cores, ranging between 1.12 g cm^{-3} in the upper layer to 1.18 g cm^{-3} at 20 cm depth.

3.1.2 Långsjön

In Långsjön the dry matter content increased deeper in the sediment, with about 5 % in the top layer and 20 % at around 20 cm (Figure 5). There was a small decrease between 12 and 13 cm down in Långsjön 1. The sediment density for all three cores in Långsjön varied between 1.02 g cm^{-3} in the upper layer to 1.05 g cm^{-3} in deeper layers.

Organic matter content was generally higher in Långsjön compared to Flaten, and varied between 30 and 50 % for all three cores. The higher organic matter content was not surprising in the upper sediment layers, since more plant residues is available before it is decomposed deeper down in the sediments.

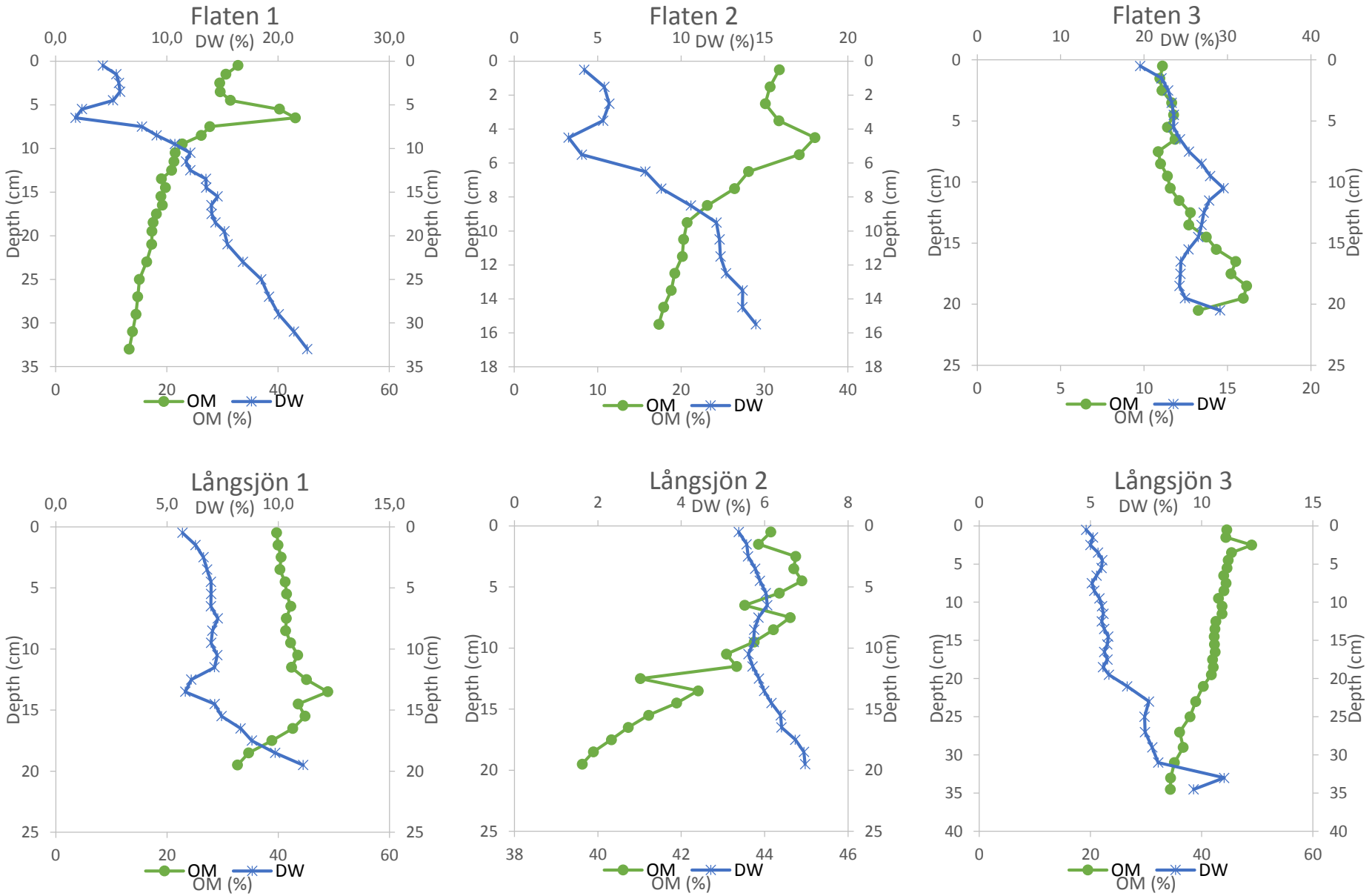

Figure 5. Organic matter content and dry sediment weight with depth in Flaten and Långsjön. Note the different scale on every axis.

3.2 Aluminium treatment

3.2.1 Flaten

The concentration of added Al, Al-P formed and total sediment P varied substantially in most cores collected from Flaten (Figure 6). The background concentration of Al for each core was estimated using deeper and shallower sediment layers which were not been affected by the treatment. For the calculation of the average Al:Al-P ratios (g m^{-2}) the above background mass of Al and Al-P in the sediment layers affected by treatment were summed (Table 3). The mobile P consists of pore water, loosely bound, and reductant soluble P and was estimated by summing measured mobile P and excess Al-P before Al-treatment. The above background mass of Al and Al-P was then summed for each sediment layer. For core Flaten 1 the sediment layers between 2.5 and 7.5 cm depth had excess Al and Al-P from treatment. In core Flaten 2 the layers between 1.5 and 5.5 cm depth, and for core Flaten 3 4.5 and 9.5 cm depth were used to determine Al and Al-P from treatment.

In core Flaten 1 there was a substantial peak in formed Al-P, Al and total sediment P in the sediments between 5 and 7 cm depth. The highest concentration in Al-P was 14.3 mg g^{-1} at 6.5 cm, and the concentration of Al at the same sediment depth was 137.8 mg g^{-1} (Figure 6). The sum of added Al between 2 and 8 cm sediment depth was 51.7 g m^{-2}, which resulted in the formation of 5.0 g m^{-2} P as Al-P. The calculated ratio of Al:Al-P was 10.4.

Core Flaten 2 was taken at a depth of 11.6 m (Figure 6). Similar to core Flaten 1, a distinct peak of formed Al-P, Al and total sediment P were found at sediment depths between 5 and 7 cm. At 5.5 cm depth the highest concentration in Al-P was measured at 3.8 mg g^{-1}. The concentration of Al at the same depth was 53 mg g^{-1}. The sum of added Al mass was 29.1 g m^{-2} between sediment layers 1 and 6 cm depth. The added Al resulted in 3.3 g P m^{-2} adsorbed to Al, resulting in a Al:Al-P ratio of 8.9.

The Flaten 3 core was collected at 8.1 meters water column depth, a more shallow part of the lake. There were peaks of Al, Al-P and total sediment P here as well, although not as high as in the other sampling sites (Figure 6). From the sediment surface until 8 cm into the sediment the concentration in Al-P was 0.10 mg g^{-1}. At 8.5 cm the concentration decrease and was 0.04 mg g^{-1} until 20 cm depth. The Al concentration was also more consistent in the sediment profile and ranged from 16 to 18 mg in the whole core. The ratio of Al:Al-P in core Flaten 3 was the highest

in Flaten with 12.4. The ratio was calculated from the sum of added Al was 9.0 g m^{-2} between 4 and 10 cm sediment depth, and resulted in 0.7 g m^{-2} of P adsorbed to Al.

In previous studies the ratio of Al:Al-P has varied between 2.2-14.5 (Rydin et al. 2000; Lewandowski et al. 2003; Reitzel et al. 2005; Huser et al. 2011; Huser 2012). The ratio in Flaten varied between 8 and 12 for the three sediment cores analyzed in this study, which is within the same range as previous studies. It is possible to estimate the total amount of P in the sediment of Flaten that was inactivated by the Al treatment. The average Al:Al-P ratio in Flaten was 10.5 and treated lake area was 40 ha, which gives 2.3 ton of immobilized P.

Recovery of Al between 74 to 23 % in Flaten and 66 % in the only core studied from Långsjön. In Långsjön the results in Al and formed Al-P was more ambiguous, and thus were two different backgrounds calculated. With the first background a ratio of 10.6 was calculated and in the second 15. Al recovery was 66 and 99 % with the first and second background estimates respectively, shown in parenthesis in table 3. This result is similar to the recovery rates found in six lakes in Washington where the recovery of Al varied from 30 to 70 % (Rydin et al. 2000).

Table 3. Sediment chemistry data with Al dose and Al:Al-P ratios for Flaten and Långsjön. For Långsjön two background estimates were calculated. The result based on the second background estimation is shown in parenthesis.

Core	Al dose (g m^{-2})	Al recovered (g m^{-2})	Al recovered (%)	Al-P (g m^{-2})	Al:Al-P (g m^{-2})
Flaten 1	70	51.7	74	5.0	10.4
Flaten 2	70	29.1	42	3.3	8.9
Flaten 3	40	9.0	23	0.7	12.4
Långsjön 3	75	50 (74)	66 (99)	4.7 (4.7)	10.6 (15)

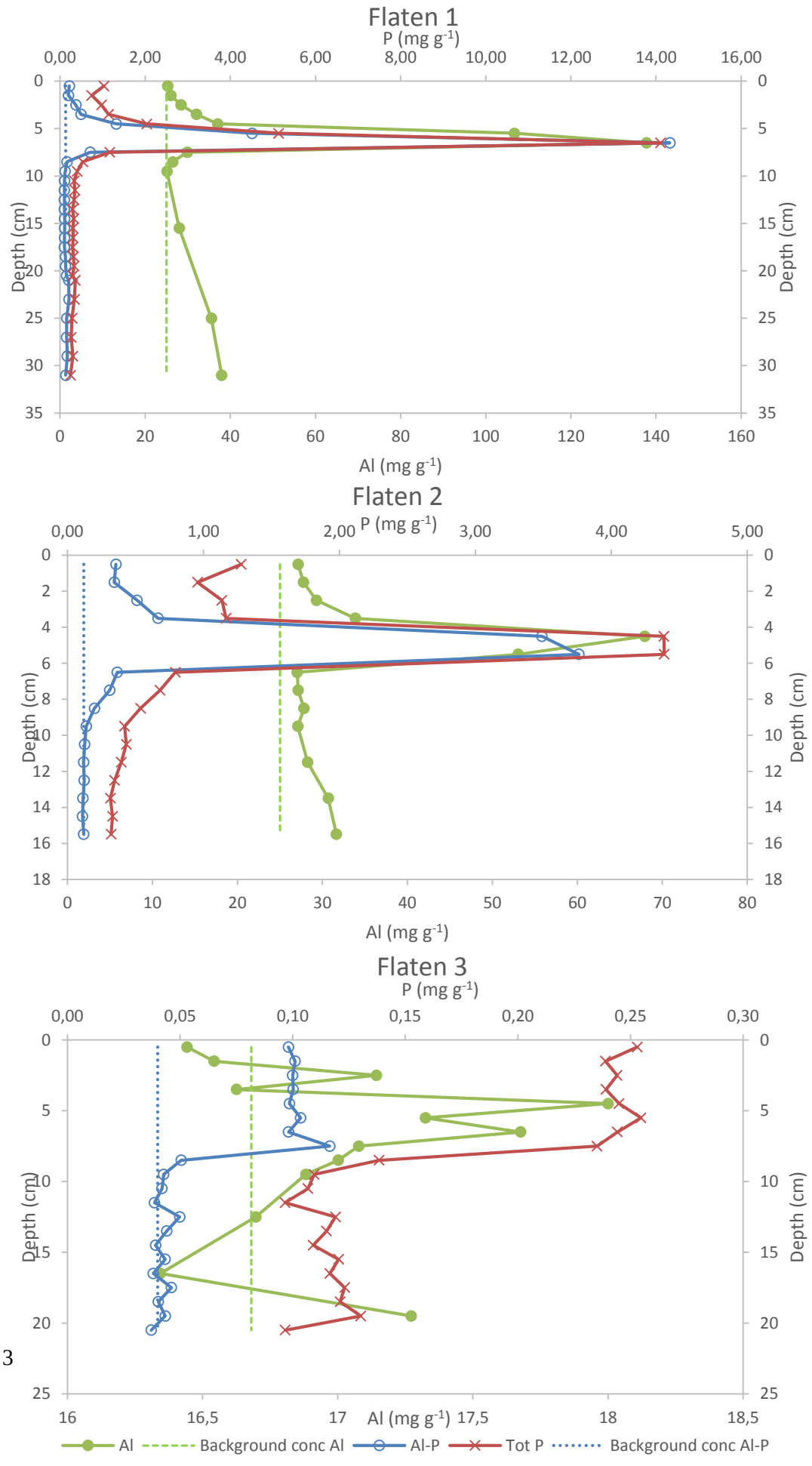

Figure 6.Concentrations of aluminium (Al) and aluminium bound phosphorous (Al-P) and total phosphorous (Tot P) in sediments from core Flaten 1,2 and 3. Note the different scale on the axis.

The cumulative amount of Al and Al-P was also calculated for Flaten (Figure 7). Lake floors below 10 meters in water column depth received the highest concentration of Al. Core Flaten 1 was collected at 12 meters depth, and as mentioned earlier core Flaten 1 had also the highest concentration in Al and Al-P. The cumulative amount of all three cores in Flaten are thus similar to the result in concentration at the same sampling sites.

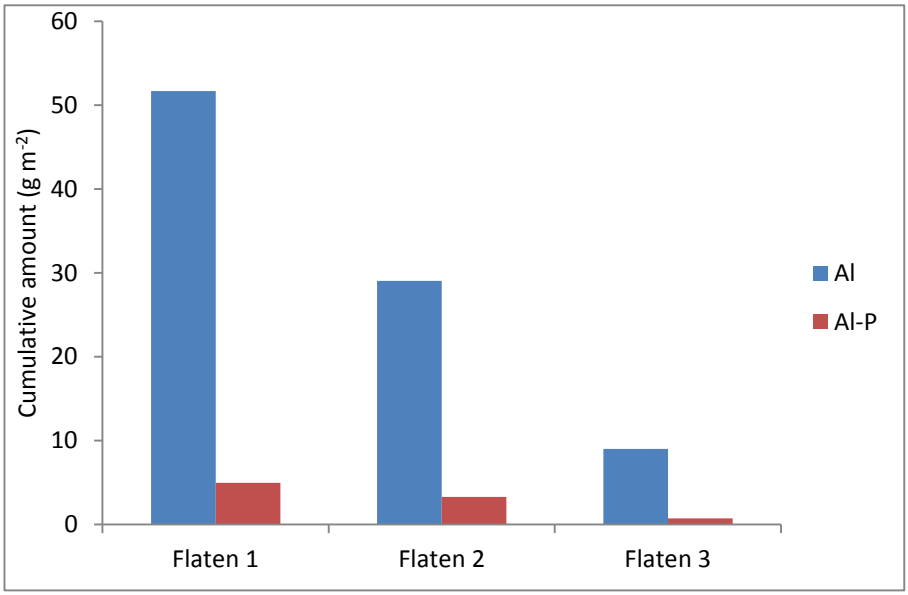

Figure 7. Cumulative amount of Al and Al-P (g m^{-2}) in core Flaten 1, 2 and 3.

The concentrations of Al and Al-P detected in the three cores in Flaten were matched with a depth map of the lake to simulate the concentration of Al and formed Al-P in the entire lake (Figure 8). This was done to give a rough estimate of how the concentration in Al-P would look after treatment. Lake floors with the same water column depth as core Flaten 1, 2 and 3 were given the same concentration as in the sampled points. It was thus expected that the concentration in Al and Al-P was higher in deeper lake parts compared to more shallow areas.

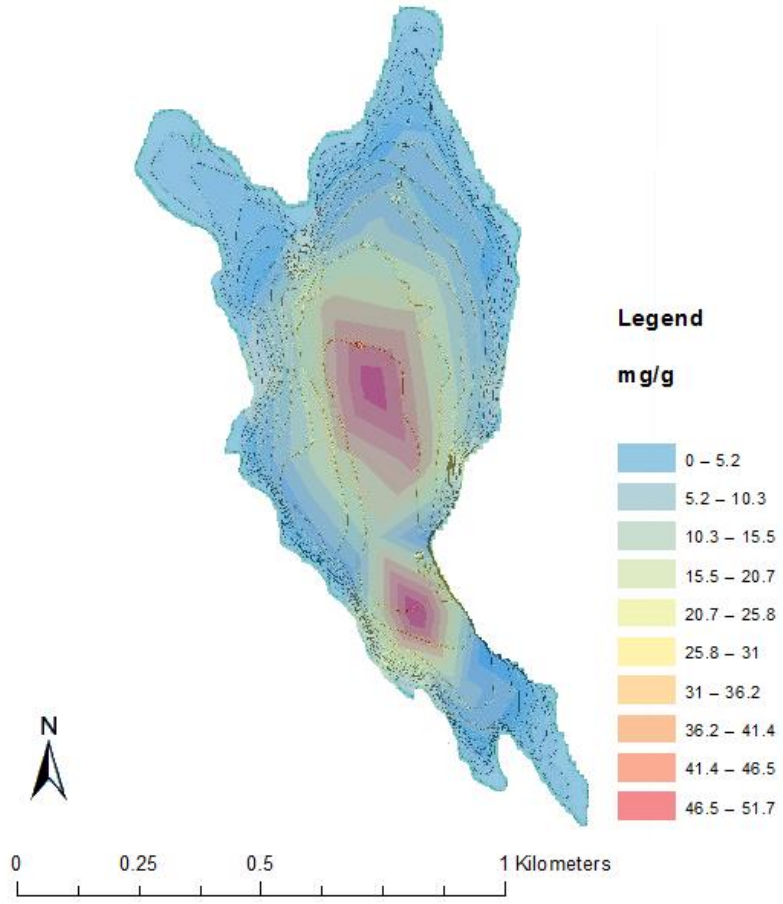

Figure 8. Simulated concentration in Al-P (mg g^{-1}) for the entire Flaten.

3.2.2 Långsjön

Evidence of added Al, Al-P formed and increased total sediment P concentrations were also seen in the core Långsjön 3 collected from Långsjön (Figure 9). Because no increase was detected in Al-P concentrations for the cores Långsjön 1 and 2, Al was not measured for these two cores. In contrast to the distinct peaks in Al-P concentrations seen in Flaten, the results for Långsjön had a more irregular pattern. The sediments seem to be completely mixed and thus the results were more difficult to interpret.

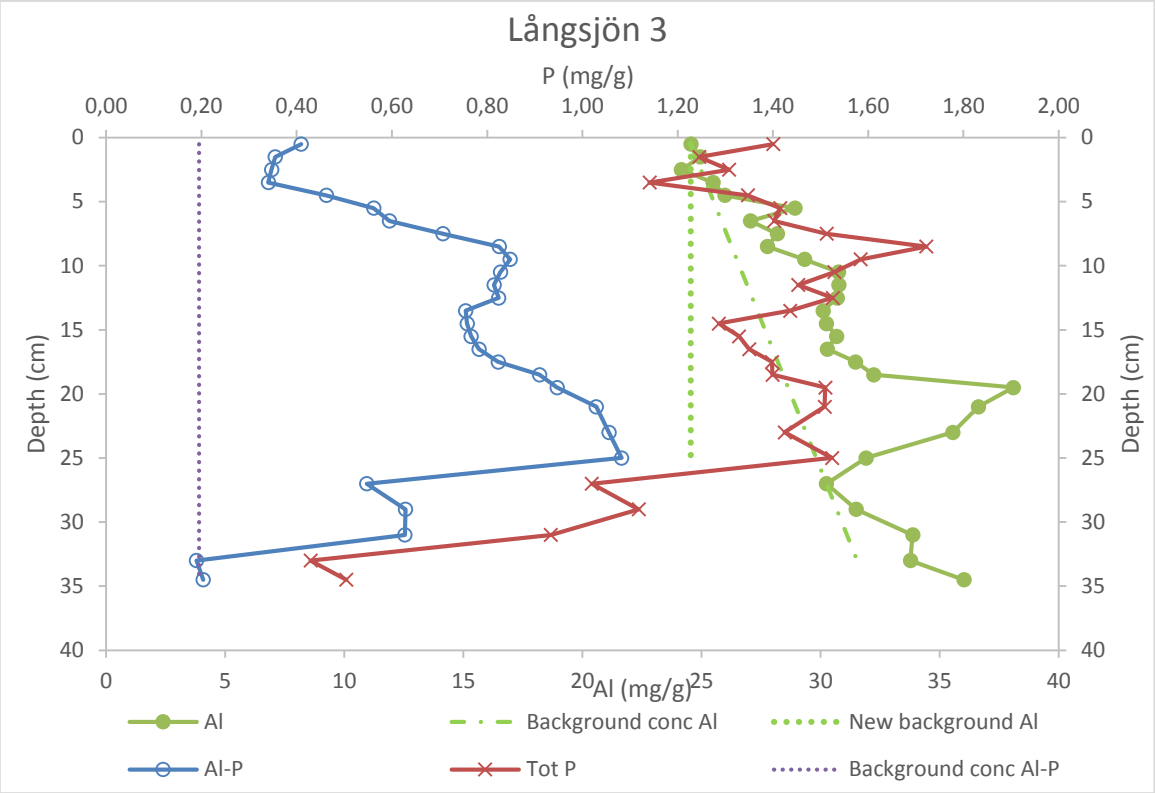

Figure 9. Concentration in aluminium (Al), aluminium bound phosphorous (Al-P), total aluminium (Tot P) and background concentration of Al and Al-P

Although not as distinct as in Flaten, two peaks in Al-P were detected. The largest peak at 25 cm sediment depth had a concentration of 1.10 mg g^{-1}. This peak is likely related to the treatments done in 1968 and 1970. The second peak was between 9 and 10 cm depth. At this peak the concentration was slightly lower compared to the one at 25 cm depth (0.85 mg g^{-1}), and is likely from the treatment done in 2006. Because of likely sediment mixing, it is difficult to estimate the sedimentation rate and thus the exact depth related to the treatment. The elevated concentrations at 25 and 10 cm sediment depth in Al and formed Al-P is however likely related to the previous treatments.

The Al concentrations follow the same pattern as the Al-P in the sediment of Långsjön. The concentration was lowest in the surface layer (0 to 1 cm) at 24.5 mg g^{-1}. Further down the sediment, the concentration increased with a peak of 38 mg g^{-1} between 19 and 20 cm sediment depth. From 20 cm depth the concentration gradually decrease until 30 mg g^{-1} at 27 cm depth.

The sum of added Al was 8.2 g m^{-2} and resulted in a formation of 1.8 g m^{-2} P as Al-P between 6 and 11 cm sediment depth. The calculated ratio in core Långsjön 3 was 10.6 (Table 3), which is within the range of ratios found in alum treated lake studies (Rydin et al. 2000; Lewandowski et al. 2003; Reitzel et al. 2005; Huser et

al. 2011; Huser 2012; Jensen et al. 2015). With a Al:Al-P ratio of 10.6 and lake area of 29 ha, the total amount of immobilized P was 2 ton. Because of the ambiguous results in core Långsjön 3 two different backgrounds were calculated. In the first background two concentrations were calculated in order to estimate the Al:Al-P ratio in Långsjön 3. The background was calculated from two sample points likely to be unaffected by the treatment and should resemble background concentration of Al. The concentration in Al from 2.5 cm and 27 cm sediment depth were chosen and an equation was constructed and fitted into the data for core Långsjön 3. The equation had the following formula:

$$y = 4.6561x - 113.82 \quad \text{(Eq. 5)}$$

The second background was based on the mean Al concentration in sediment layers between 1 and 3 cm depth. With this background concentration in Al the ratio of Långsjön core was changed from 10.6 to 15.

3.2.3 Other fractions

In the P fractionation procedure the loosely bound P (in the figures labelled pore water) and P bound to phases of Fe, Ca and organic matter are also measured apart from the P bound to Al.

Flaten

In core Flaten 1, only the fractions of loosely bound P and Fe-P seemed to be affected by the treatment (Figure 10). Both fractions had an increase in concentration at the same depth as the Al-P fraction, between 5 and 7 cm sediment depth. Core Flaten 2 had an increase in Fe-P and Org-P at the same sediment depth as the increase in Al-P between 4 and 6 cm.

All the fractions apart from Al-P seemed to be unaffected by the treatment in core Flaten 3. The concentrations for all fractions were slightly smaller in core Flaten 3 compared to the two other cores. The exception however is Ca-P which had the highest concentration in core Flaten 3. This core was taken at 8 m water column depth, and is thereby the shallowest core taken in Flaten. The higher concentration could be a result from more abundant biota, with Ca in their shells, living in the shallow water depth.

Långsjön

Ca-P in core Långsjön 1 was likely the only fraction affected by the treatment in Långsjön (Figure 10). This fraction had an increase in concentration between 5 and 6 cm sediment depth. The Org-P fraction had the highest concentration in

Långsjön and decreased with sediment depth. This would be expected when the content of organic matter is usually higher in the upper sediments. Långsjön is considered eutrophic and thus has a high primary production which contribute to more detritus and organic matter in the sediments. It is interesting that mobile P is increasing at the surface. This could be due to a continuous high external loading or that not enough Al was added.

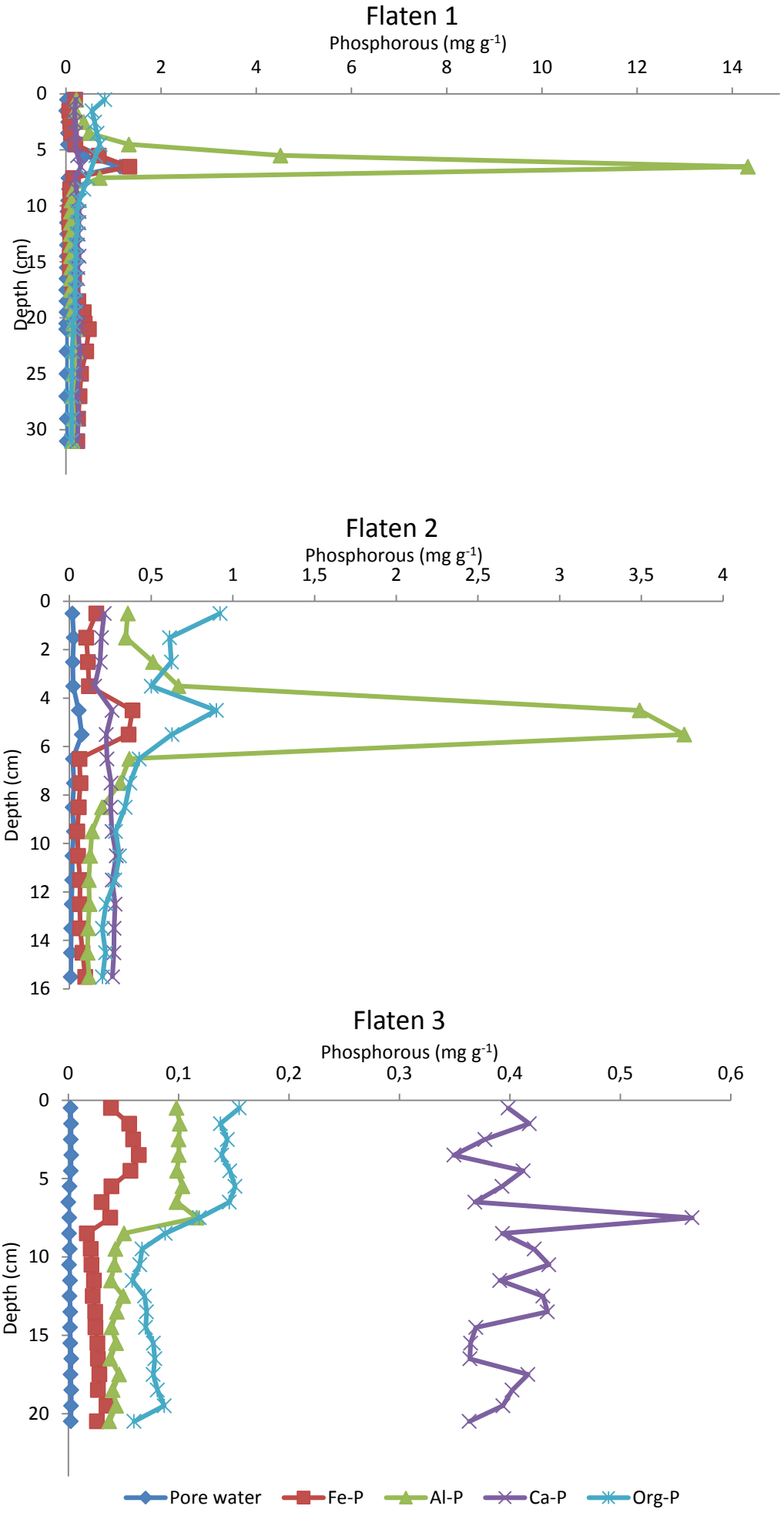

Figure 10. Concentration in loosely bound phosphorous (Pore water), P bound to iron (Fe-P), aluminium (Al-P), calcium (Ca-P) and organic matter (Org-P) in Långsjön.

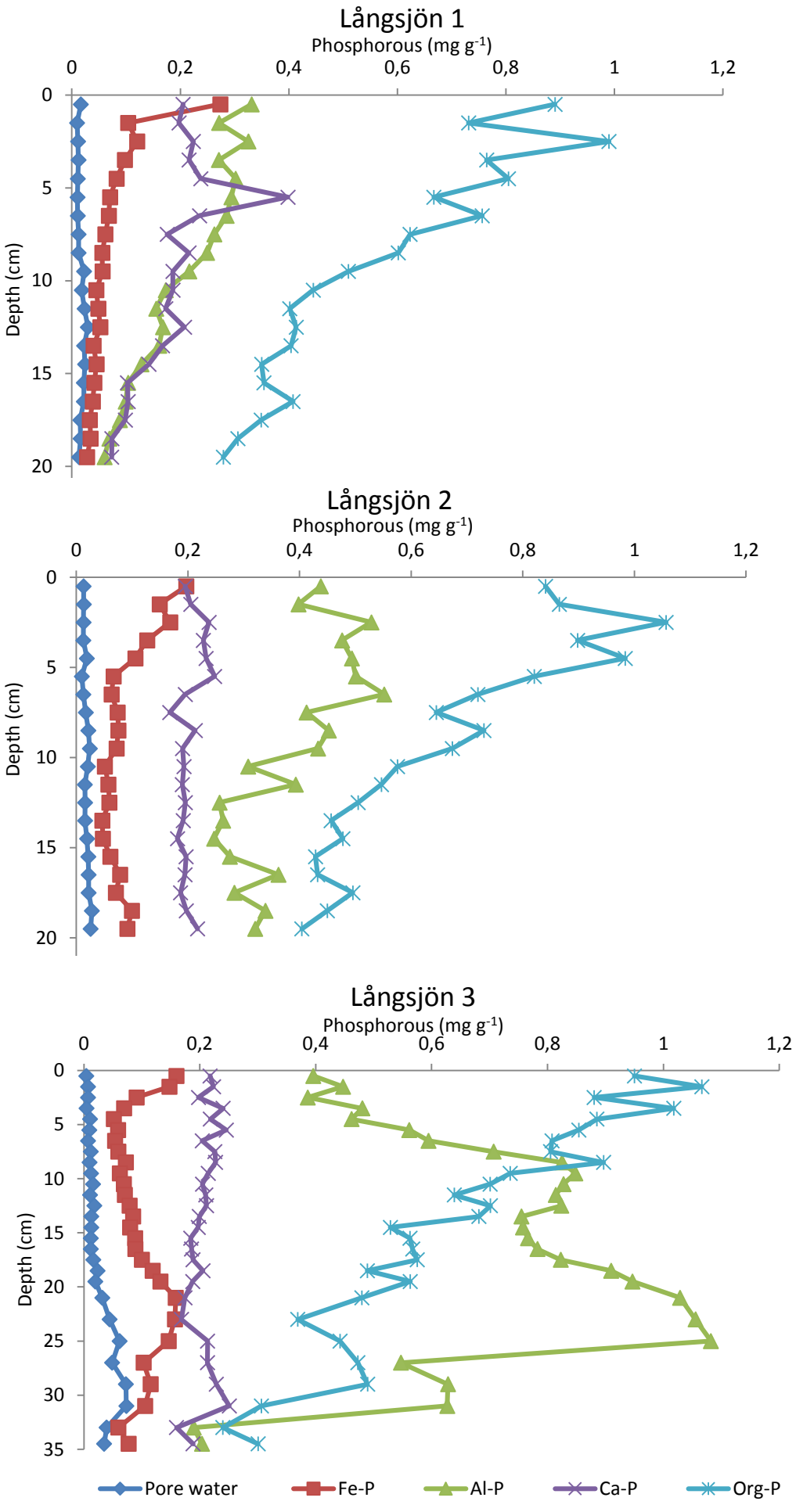

Figure 11. Concentration in loosely bound phosphorous (Pore water), P bound to iron (Fe-P), aluminium (Al-P), calcium (Ca-P) and organic matter (Org-P) in Långsjön.

3.2.4 Costs of different application methods

The costs associated with Al treatment can be divided into three main components; engineering and dosing, the Al chemical and application. Unfortunately for this study, no data was available for the application costs for the two methods to compare. It is possible that the injection application is more technically advanced and would thus be more expensive to execute. The total cost for the injection application done in Flaten in 2000 was 2.5 million SEK, which in 2014 was equivalent to 3 million SEK. Total restoration cost for Långsjön was in 2014 3.3 million SEK (3 million SEK in 2006).

To compare the cost efficiency of the two application methods, the total amount of formed Al-P was calculated from the applied dose in g Al per m^{-2} and Al:Al-P ratio of each lake (Table 4). The total cost of the treatment was then divided with total amount of formed Al-P, to get the cost per formed kg of Al-P. For the calculation of cost per kg Al-P, the treatment area was used and not the entire lake area. The value in parenthesis in total Al-P in kg and cost per kg Al-P for Långsjön is calculated with 15 as Al:Al-P ratio.

Table 4. Dose, total amount of formed Al-P and costs for Flaten and Långsjön compared with lakes in Minnesota, USA treated with surface application.

	Area (ha)	Treated area (ha)	Dose (g Al m^{-2})	Total Al-P (kg)	Total cost (million SEK)	Cost per kg Al-P (SEK)
Flaten[a]	63	40	61	3660	3	1290
Långsjön[b]	29	29	75	2050 (1450)	3.3	1608 (2276)
Harriet[c]	45	45	11	2637	1.3	490
Cedar[c]	70	60	27	2244	2.3	1170
Calhoun[c]	180	130	42	15095	2.3	210
Isles[c]	44	26	18	1624	1.1	1180

Based on data from [a] Värnhed (2005) [b] Värnhed (2009) [c] Huser et al. 2011

The costs per kg formed Al-P for both Flaten and Långsjön are within the same range as the Minnesota lakes treated with surface application, although on the higher end. The average cost is higher for injection treatment, one reason for this could be that injection treatment takes more time to execute. In comparison with dose to cost per ha, Långsjön diverged much compared to the other lakes. This would be expected since the total costs for Långsjön were high compared to its small area and large Al dose. Depending on the accuracy of the Al:Al-P ratio, a comparison between costs per formed Al-P would be a more direct method to test the cost efficiency between the two application methods.

4 Discussion

In this study the binding efficiency of P by Al has been compared in two different treatment methods. In the traditional method the Al salt is applied on the lake surface where it precipitates down towards the sediments were it binds to the stored P. The newer injection method was developed in an attempt to make the binding more efficient since the Al is injected directly into the sediments. After the injection treatment the concentration of water column P declined in both Flaten and Långsjön. In Flaten the seasonal average concentration of TP decreased from 40-50 µg L^{-1} to 10 µg L^{-1}. The concentration in Långsjön decreased from 100 µg L^{-1} to 27 µg L^{-1}. The average ratio of Al:Al-P was 10.5 in Flaten and 7 in Långsjön. These results are similar to previous studies with surface application, which would suggest similar binding efficiency for both application methods. The results will be discussed further in this chapter.

4.1 Binding of P by Al

4.1.1 Shallow lakes (Långsjön)

It has previously been suggested treatment longevity for Al application in shallow polymictic lakes is generally lower compared to deeper dimictic lakes. The management of trophic states is also usually more difficult in shallow lakes (Cooke et al. 2005). Huser et al. (2015a) showed however that increased sediment mixing could improve the binding efficiency of P by Al also in shallow lakes. The results for core Långsjön 3 were more ambiguous when compared to Flaten. There was no significant peak as seen in Flaten, instead a more irregular pattern. One reason for these results is mixed sediments caused by benthic feeding fishes such as carp or bream. Due to the mixing, it is difficult to say if the sediments are in the same layers as when they were deposited, which makes it more difficult to calculate the amounts of Al and Al-P in the sediment due to treatment. Apart from mixing by fish, wind turbation might also be a cause for mixed sediments. The ratio of Al:Al-

P found in core Långsjön 3 was 7.0, which was slightly lower compared to the ratios detected in Flaten. The low ratio might be due to mixing of the sediments when the Al salt was injected. That would result in a more efficient P adsorption by the amorphous Al floc before it settled and started to crystallize, losing binding capacity.

Even though the results from core Långsjön 3 were more difficult to interpret, a ratio of 7.0 is lower compared to rates found in some shallow polymictic lakes in Denmark, such as Lake Kollelev and Glumsø where the Al:Al-P ratio 3 years after treatment were 16 and 18 respectively (Jensen et al. 2015). These high ratios could be due to incomplete saturation of the Al floc, and might decrease with time allowing the Al floc to saturate. The injection method should in theory decrease the time for contact between Al and P compared to a surface application technique. This is because the Al floc settles on top of the sediment and slowly mixes into the sediment by wave turbulence or benthic activities after the surface application. The increased sediment mixing occurring when the PAC was injected could have proven to be more efficient with respect to P inactivation compared to previous surface applications method in Långsjön. This is however difficult to say for certain, especially when looking at the results for Flaten.

4.1.2 Deep lakes (Flaten)

The core taken at the deepest sampling point in Flaten 1, had the highest concentration of aluminium bound P. The significant peak in concentration and amount of Al and Al-P would be from the treatment done in 2000. There was a substantial difference in concentration of Al-P between core Flaten 1 (14.3 mg g^{-1}), core Flaten 2 (3.8 mg g^{-1}) and core Flaten 3 (0.12 mg g^{-1}). One explanation could be the morphology of Flaten. The steep bottom slopes could have contributed to a transportation of the Al floc to deeper parts. Huser (2012) showed the importance of lake morphology as a significant contributor of Al translocation and potential aging of Al in the absence of P, which limits the binding capacity of the Al over time. In core Flaten 2 for instance, the wet sediment density between 4 and 5 cm sediment depth, were the maximum concentration in Al and Al-P was found, was low (1.01 g cm^{-3}). This would also suggest that the sediments are more easily transported by turbulence or wave action to deeper parts of the lake (Huser 2012).

The ratio in Al:Al-P was 10.4 in core Flaten 1, 8.9 in core Flaten 2 and 12.4 in core Flaten 3 (average for whole Flaten was 10.5). A higher ratio in core Flaten 3 was detected. In urban areas storm water can transport Al to lakes, making detection of stabile background difficult (Rydin et al. 2000). Particulate Al in storm water might have been washed and mixed into the sediments where core Flaten 3

was sampled. There may have also been less P to bind to the Al here, allowing the Al to crystalize in the absence of P. A lower ratio in Flaten 1 and 2 could also be due to a saturated Al layer. The amorphous Al floc will crystalize within time, the sorption capacity of P will decrease (Berkowitz et al. 2006).

The Al:Al-P ratios in Flaten and Långsjön were within the same range as found in other studies (Rydin et al. 2000; Lewandowski et al. 2003; Reitzel et al. 2005; Huser et al. 2011; Huser 2012 and Table 5). This would suggest that the efficiency of the two different application methods do not diverge much. The ratio between added Al and formed Al-P is affected by the amount of added Al and thus how much P is bound to the Al. There are also differences in chemical, physical and biological processes in the sediments, and which make ratios difficult to compare (Reitzel et al. 2005). Differences in morphology, hydrology and water chemistry will also affect the ratio (Huser et al. 2015a). In previous studies there are different conditions and circumstances in the Al treated lakes compared to the lakes in this study. Factors like differences in lake morphology and size; Al dosage method (alkalinity vs mobile P in sediments); which Al chemical used (alum vs PAC) to mention some, which should be taken into consideration when making the comparison.

Table 5. Al treatment information in stratified (A) and polymictic (B) lakes. Dose method indicates either mobile sediment P (S) or alkalinity or water column P (W). The abbreviations MN and WA stands for Minnesota and Washington respectively. Sediment core samples and thus the Al:Al-P ratio were collected and determined in different years; Sønderby in 2003, WA and MN lakes in 2000, Süsser See between 1999 and 2002.

Lake	State	Country	Treatment year	Surface area (ha)	Mean depth (m)	Al dose (g Al m^{-2})	Al:Al-P (weight)	Dose method
A								
Flaten	Stockholm	Sweden	2000	63	7.4	61	10.5	S
Sønderby[a]	Fyn	Denmark	2001	8	2.9	31	7.5	S
Calhoun[b]	MN	USA	2001	180	10.6	42	5.0	S
Cedar[b]	MN	USA	1996	68	6.1	27	8.4	W
Harriet[b]	MN	USA	2001	138	9.8	32	1.9	S
Ballinger[c]	WA	USA	1990	41	5.0	23	9.9	W
Medical[c]	WA	USA	1977	64	9.7	122	11.4	W
B								
Långsjön	Stockholm	Sweden	2006	29	2.2	75	7.0	S
Süsser See[d]	Sachen-Anhalt	Germany	1977-1992	269	4.3	100	2.1	W

Isles[b]	MN	USA	1996	42	2.7	18	4.9	W
Campbell[c]	WA	USA	1985	150	2.4	26	10.8	W
Erie[c]	WA	USA	1985	45	1.8	20	11.5	W
Phantom[c]	WA	USA	1990	24	6.4	28	9.8	W

Based on data from [a] Reitzel et al. (2005), [b] Huser et al. (2015c), [c] Rydin et al. (2000), [d] Lewandowski et al. (2003)

In some previous studies the ratio of Al:Al-P has varied between 2 and 14. (Table 5). Calhoun, Cedar Harriet and Isles are part of the Minneapolis chain of lakes (COL) and were studied by Huser et al. (2015a). The lakes are similar to Flaten and Långsjön; they are also situated in a residential recreational area are part of a recreational area. Flaten, Långsjön and Sønderby were treated with PAX and the other lakes presented in Table 4 with alum.

In general, although more different parameters are diverging between studies where surface application and injection application have been used, the results presented in this study would suggest that the efficiency between the two methods is within the range of previous treatments. Flaten was however towards the higher end compared to previous surface treatments. Another reason for the similar binding ratio in both methods could be that the Al floc applied in surface application has easier access to P in the water column after settling to the sediment surface. Meaning that the Al floc from surface application has two sources of P; both from the sediments and water column whereas the injected Al has to wait for the P to reach it.

4.1.3 Uncertainties

When conducting laboratory experiments, there is always the possibility of uncertainties and errors. The background concentration of Al was estimated in all cores in both lakes, and based on sediment layers that seemed to not be affected by the treatment. The uneven pattern in concentration of Al and formed Al-P in core Långsjön 3, made the estimation of background concentration of Al more difficult. The fluctuating concentration in Al was probably due to Långsjöns' urbanized location. Two backgrounds were calculated in different ways to manage the fluctuating concentrations. In order to estimate the first background concentration of Al in Långsjön an estimation based on two sample points was done. The second background was calculated as a mean of samples between 1 and 3 cm depth. Due to the urbanized location of Långsjön particulate Al from e.g. storm water might have been washed into the lake, and it is thus difficult to know if this Al is binding

to P or not, and might mask the effects of the treatment. This makes the results more uncertain, but seemed to be the best option with the data available. With two different backgrounds in Al concentration, the Al:Al-P ratio did also change from 10.6 to 15. The different ratios does also affect the cost efficiency, where the higher ratio suggests lower binding efficiency, and thus the costs per kg formed Al-P is higher with a higher ratio.

Other uncertainties with this study is that only three cores from each lake were sampled and in Långsjön only one core was analyzed for Al. These limited amount of data will of course make the results more uncertain.

4.2 Effectiveness of treatment

4.2.1 Water quality pre and post treatment

In both Långsjön and Flaten the concentration in TP decreased in the water body after treatment. For Flaten, the moving average of TP in August prior to treatment was 14 µg L^{-1} (Figure 12). In 2014, the concentration in TP was 10 µg L^{-1}, and Flaten is thereby reaching the water quality goal set by the Swedish Environmental Protection Agency (Stockholm Stad 2015a). It has been 15 years since the lake was treated when this study was conducted, and Huser et al. (2015a) estimated the longevity of TP in Flaten to be 41 years. Welch and Cooke (1999) found the longevity of Al treatment to last between 1 to 11 years in polymictic lakes and between 5 and 20 years in dimictic lakes. The Al dose for the reviewed lakes by Welch and Cooke were determined based on alkalinity and not the amount of mobile P in the sediment, as was done in Långsjön and Flaten.

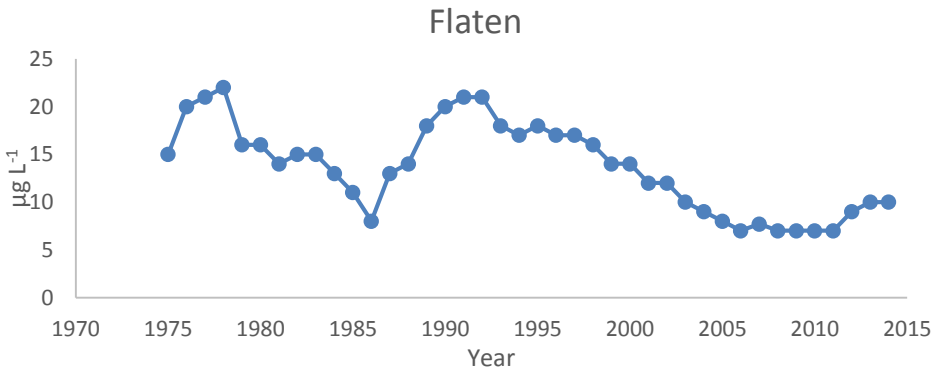

Figure 12. Moving average of surface TP in August from 1975-2014 in Flaten. Adapted from Stockholm stad 2015a.

In a study by Huser et al. (2015c) the urban shallow, polymictic Lake Isle in the Minneapolis Chain of Lakes was treated with alum, and the longevity of the treatment lasted about 4 years. In 2005, one year prior to the treatment in Långsjön, the concentration of moving average of August TP was 110 µg L-1 (Figure 13). After the treatment it slowly decreased, and reached its lowest concentration in 2011 (28 µg L-1). From 2012 to 2014, the concentration has slowly increased and was 52 µg L-1 in August 2014. 52 µg L-1 is considered higher than current water quality standards allow according to the Swedish Environment Protection Agency, and Långsjön is thus not meeting the current water quality goals for August TP values (Stockholm Stad 2015b).

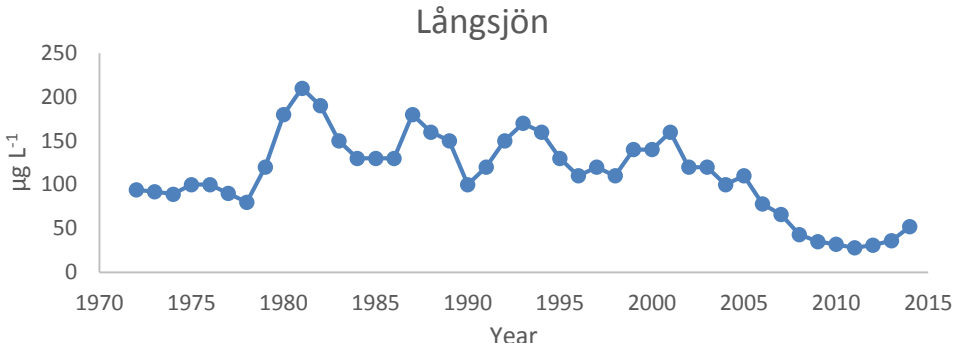

Figure 13. Moving average of surface TP during August from 1970-2014 in Långsjön. Adapted from Stockholm Stad 2015b.

In Lake Sønderby the concentration in TP started to increase over the 10 following years after treatment (Jensen et al. 2015). The study by Huser et al. (2015a) estimated longevity of TP in Långsjön to 8 years. When this study was done, it has been 9 years since the Al treatment in Långsjön. The Al dose was substantial higher in Långsjön compared to Lake of the Isle (75 versus 18 g Al m^{-2}, respectively), which might explain why the treatment seemed to have lasted longer in Långsjön compared to Lake of the Isle. Reasons why the treatment did not last longer in Långsjön could be a continued high amount of external nutrient load. Huser et al. (2015a) found that the longevity of an Al treatment increased with greater the water column depth and watershed area relative to lake area, which would then suggest that it is expected that the treatment seem not to have lasted longer in Långsjön. However this could just be a factor representing the fact that lower Al doses were added to shallow lakes in the past due to lower availability of alkalinity.

The effect on water quality from treatments done in 1968 and 1970 using surface application did not last long. A continued high input of external nutrients com-

bined with too low of an Al dose, led to too little reduction of mobile P in the sediment. It is difficult to make a reasonable comparison between the methods used at Långsjön because the conditions during the treatments were too different. For Långsjön though the injection application seems to be more efficient, but a higher dose of Al was added. With a higher dose more P can be bound by Al which reduced the chance for aging Al in the absence of P.

4.2.2 Binding efficiency

The injection method was thought to have a more efficient binding capacity of P by Al. Together with less impact on the aquatic biota in the water column, it was considered to be a better treatment method to reduce internal loading in eutrophic lakes. On the contrary to the hypothesis, this study could conclude a similar binding efficiency between injection and surface application. In different Al treated lakes are water residence time and water column stability important factors which affects the longevity of the treatment (Huser et al. 2015a). Which kind of Al dosing method, such as based on water alkalinity or the amount of available mobile P in the sediments, might also lead to either under- or over-dosing of Al and thus affect the longevity.

Benthic feeding fishes are another factor which could affect the binding efficiency. Huser et al. (2015b) showed that 5 to 16 cm of the sediment can be mixed by carp and other benthic feeding fishes. The occurrence of benthic feeding fishes affect the quality of the water and potentially more mobile P can be released into the water column because of more sediment interacting with the water column (Huser et al. 2015a). Both carp and bream are present in Flaten and Långsjön and could thus affect the efficiency in both lakes. The feeding activities of fishes in Långsjön might have contributed to the increase in TP.

As briefly mentioned before, the amorphous flock of $Al(OH)_3$ will age with time and the binding capacity of Al to P decreases. The ratios presented in the study is based on a mean ratio in the upper 10 centimeter of the sediments. The Al:Al-P ratio was observed to fluctuate in the whole sediment profile. This would suggest the formation of Al-P was not at maximum and could be due to aged and crystallized $Al(OH)_3$, or more time is needed for mobile P to saturate all binding sites.

In Flaten the average recovery of Al in all three cores was 46 % of the Al dose. In Långsjön Al was only measured in one core, with a recovery of 11 %. Because both lakes were treated with injection application, the Al floc should in theory not been affected by translocation. Flaten has however steep slopes and since the den-

sity of the Al floc is low, it is still possible that the Al has moved to deeper parts of the lake. Långsjön does not have any steep slopes, but since only one core was analyzed for Al, it is difficult to draw good conclusions of the low recovery in Långsjön.

4.3 Main differences between the two treatment methods

One reason for the development of the injection method by the developers was to increase the efficiency of P binding by Al. In this study however, the binding efficiency was similar for both methods. Another reason for the development of the injection application method was to minimize the effects in the water column. It has been discussed prior to the treatment in Flaten and Långsjön that the injection application was chosen as it was considered to affect the lake living organisms less compared to surface application. In this study the effects on organisms living in the water column and in the sediments have not been investigated. In 2011 when fish species where monitored in both lakes, Flaten received high ecological status and Långsjön a good status (Fränstam 2011). It is thus difficult to say if injection application is better compared to surface application with regards to the organisms in Al treated lakes. Short-term effects observed in previous studies with surface application are likely avoided with injection application.

Regardless of the method chosen, water quality has generally improved when using both methods, which would benefit aquatic living organisms. Improved oxygen conditions due to more oxygen in the upper sediment layer and changed phytoplankton composition can have positive effects on aquatic living organisms (Smeltzer et al. 1990). In Lake Morey this was observed where more species were discovered in the benthic community a few years after alum treatment compared to the year prior treatment (Smeltzer et al. 1999). There was however a 90 % decline in the benthic community the following year of treatment, but the community fully recovered two years after treatment (Smeltzer et al. 1999). Studies on how benthic organisms are affected by injection application would be recommended for the future especially since the knowledge on Scandinavian species is limited (Rydin 2006).

Because of limited amount of data, the costs were only compared to four other lakes that had been treated with surface application. The results indicated that the costs per kg formed Al-P for Flaten and Långsjön did not differ much; the costs were not higher nor lower compared to the other lakes. When taking a mean of each dosing method, the injection method was more expensive. This is not surprising because more worker-hours are needed to complete an injection treatment. The

costs for injection may be more expensive because of lower alkalinity in the sediments. There are less water in the sediments compared to the water body and the alkalinity is thus lower in the sediments. It is possible that the treatment costs could be greater for the injection application because buffered forms of Al are needed. The efficiency was however based on the estimated ratio for each lake, and with the ambiguous results for Långsjön the cost efficiency for this lake may not be completely accurate.

Another problem with the comparison is the lack of data to differentiate between the Al chemical and application costs for the two methods. Would be interesting in future studies if the separate costs for the treatments were compared individually. Alum and PAC have different chemical properties which affect the differently. Alum contains a high amount of sulfate which together with Fe can form FeS, iron sulphide, which might decrease P binding capacity in the sediments (Hansen et al. 2003).

5 Summary and conclusions

In this study the binding efficiency and costs for two different application techniques were compared. From previous studies and this one, it can be concluded that both methods reduce water column P through a reduction in sediment P release. It is difficult, however, to compare the effectiveness of the different measures. This is mainly due to inadequate monitoring measures; usually only TP in surface water is measured which does not distinguish between different forms or potential sources of P. The results presented in this study also indicate that the binding efficiency of both methods is similar, and the hypothesis that binding efficiency would be greater using the injection method was thus rejected. Although the mixed sediments in shallow Långsjön made the results more difficult to interpret, the ratio found was lower compared to Flaten. Compared to previous studies, the ratio was on the higher end however. With the few lakes included in this study, it did not appear that cost difference between the two methods was great. The cost per kg formed Al-P seemed to be in the range of previous treatments. The mean costs was higher for injection compared to surface application.

The injection application was a development of the surface application method which has remain relatively unchanged since the first treatments in the late 1960s. One of the main reasons for the development was that the surface application method was considered to be a harsh method because the entire water column is affected. As mentioned earlier, when monitored in 2011 the fish community was considered good in both lakes. As of yet, no studies have been done to investigate the benthic biota in Långsjön and Flaten since they were treated. Since this study did not observe the effects on the aquatic and benthic biota of the two methods are difficult to compare. Short term effects in the water column from previous studies are most likely avoided when using the injection method. As a recommendation for the future, more studies should be conducted to establish if one of the methods is more preferable. This would be particularly interesting for shallow lakes.

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